Electrochemical Parameter Identification for Lithium-ion Batteries on Separated Time-scales

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\textsc{ABSTRACT}

Lithium-ion batteries (LIBs) play an essential role in the energy sector and have been widely deployed in recent years. Generally, LIBs are managed in model-driven manners, leading to the need for parameter identification. However, as an electrochemical system, the battery contains various parameters while the measurements are mainly the current and voltage, inducing an inherent ill-conditioned identification problem. A flexible and lightweight parameter identification framework, including the test, model, and algorithm, is proposed in this work. Electrochemical parameters are grouped by time-variant features and identified on separated time-scales. Parameters with slow dynamics are identified in a hybrid data-driven and model-driven approach based on the data of a quasi-static test covering the partial SOC range. Parameters with fast dynamics are identified using a specifically designed sensitivity-oriented stepwise optimization algorithm based on the data of a dynamic test consisting of a series of constant current (CC) pulses. The mixed impacts of different parameters can be decoupled and the time costs of the test and computation can be reduced. Specifically, it takes a few hours to identify slow dynamic parameters and a few minutes to identify fast dynamic parameters. Numerical experiments on a typical LiNCM battery at different life stages are conducted. The results show that the identification accuracy of crucial parameters can reach over 95%, and the battery model error is reduced below $2 \times 10^{-3}$ V.

\section{1. Introduction}

With the rapid development of renewable energy in recent years, lithium-ion batteries (LIBs) have received more concerns. They are regarded as an essential option to stabilize the increasing volatility in power grids \cite{1}. However, when providing frequency regulation or peak shaving services, LIBs suffer from continuous degradation stress and sometimes even encounter severe conditions such as thermal runaway, indicating the necessity of monitoring battery characteristics \cite{2}. Theoretically, the LIB can be treated as an electrochemical system whose characteristics are determined by a group of parameters with concrete physical or chemical meanings. Thus, a practical identification method for these parameters is vital to the management of LIBs in real-world applications. On the contrary, the lack of information on crucial parameters may increase safety risks, e.g., the LIB storage system explosion in dahongmen, Beijing, in 2021 \cite{3}, was due to the detonation of flammable gas in some weak batteries operating at unreasonable points.

For energy storage equipment in the power sector, measurements of the LIB commonly include the current and voltage. Electrochemical parameters of the battery are then identified based on the measured data. However, the identification is challenging at both the theoretical level and application level. Theoretically, the battery is viewed as a single-input (current) and single-output (voltage) system with multi-parameters whose impacts are mixed up to form the final output. Thus, the identification is inherently an ill-conditioned problem. Directly identifying all parameters together may yield a solution that fits the output well but is actually unreasonable and lacks physical significance \cite{4}. At the application level, the battery needs to be tested under diverse current profiles to enlarge the set of observable parameters as much as possible, which can be time-consuming. Meanwhile, classic electrochemical models, e.g., the pseudo-two-dimension (P2D) model, are complex and might make the model-driven search for optimal parameters hardly be practical due to the huge computational burden.

The identification of electrochemical parameters has become a research hotspot recently. Generally, the identification involves three key points, test design, parameter determination, and algorithm development.

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Nomenclature

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\begin{align*}
\delta_f^+ & \quad \text{SEI/CEI film thickness over active materials in the negative and positive electrodes (nm).} \\
\kappa & \quad \text{Ionic conductivity of the electrolyte (S/m).} \\
\rho^+ & \quad \text{Density of active materials in the negative and positive electrodes (kg/m}^3). \\
\sigma_f^+ & \quad \text{Electrical conductivity of SEI/CEI over active materials in the negative and positive electrodes (S/m).} \\
\sigma_s^+ & \quad \text{Electrical conductivity of active materials in the negative and positive electrodes (S/m).} \\
\varepsilon_e^+ & \quad \text{Volume fraction of the electrolyte in the negative and positive electrodes and the separator.} \\
\varepsilon_s^+ & \quad \text{Volume fraction of active materials in the negative and positive electrodes.} \\
A^{sep} & \quad \text{Projected area of the negative and positive electrodes and the separator (m}^2). \\
c_e^+(x,t) & \quad \text{Li}^+ \text{ concentration of the electrolyte at time } t \text{ and thickness } x \text{ in the negative and positive electrodes (mol/m}^3). \\
C_Q & \quad \text{Battery capacity (mAh).} \\
c_s^+(x,t) & \quad \text{Bulk-averaged Li}^+ \text{ concentration of active materials at time } t \text{ and thickness } x \text{ in the negative and positive electrodes (mol/m}^3). \\
c_e^+(x,t) & \quad \text{Surface Li}^+ \text{ concentration of active materials at time } t \text{ and thickness } x \text{ in the negative and positive electrodes (mol/m}^3). \\
D_e & \quad \text{Diffusion coefficient of the electrolyte (m}^2/s). \\
D_s & \quad \text{Diffusion coefficient of active materials in the negative and positive electrodes (m}^2/s). \\
I(t) & \quad \text{Applied current to the battery at time } t \text{ (A).} \\
k_r^+ & \quad \text{Reaction rate coefficient of reactions in the negative and positive electrodes (A} \cdot \text{m}^2/\text{mol}^{1.5}). \\
L^{sep} & \quad \text{Thickness of the negative and positive electrodes and the separator (m).} \\
M^+ & \quad \text{Molecular mass of active materials in the negative and positive electrodes (kg/mol).} \\
R_t & \quad \text{Contact resistance of the current collector (} \Omega). \\
R_f^+ & \quad \text{SEI/CEI film resistance over active materials in the negative and positive electrodes (} \Omega \cdot \text{m}^2). \\
R_r^+ & \quad \text{Active particle radius (m).} \\
t_0 & \quad \text{Ion transference number of the electrolyte.} \\
U_{\text{OCV}}^+ & \quad \text{Equilibrium potential functions of reactions in the negative and positive electrodes (V).} \\
V(t) & \quad \text{Battery voltage during operating at time } t \text{ (V).}
\end{align*}
\]

Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| CC           | Constant current. |
| CCCV         | Constant current constant voltage. |
| CEI          | Cathode electrolyte interphase. |
| DST          | Dynamic stress test. |
| EIS          | Electrochemical impedance spectroscopy. |
| GA           | Genetic algorithm. |
| GITT         | Galvanostatic intermittent titration technique. |
| HPPC         | Hybrid pulse power characterization. |
| LIB          | Lithium-ion battery. |
| MAE          | Mean absolute error. |
| OCV          | Open-circuit voltage. |
| P2D          | Pseudo-two-dimension. |
| PSO          | Particle swarm optimization. |
| SEI          | Solid electrolyte interphase. |
| SOC          | State of charge. |
| SSO          | Sensitivity-oriented stepwise optimization. |

Test design is the prerequisite of identification. Ref. [5] adopted commonly-used standard tests, including the static capacity test, hybrid pulse power characterization (HPPC), resistance test and dynamic stress test (DST). In a laboratory environment, the electrochemical impedance spectroscopy (EIS) can also be conducted [4, 6]. A few studies also designed specific current sequences for the test. Ref. [7] designed a current profile composed of several hybrid pulses with different amplitudes and durations; the entire test lasted near 20 hours. Ref. [8] designed the low-rate test, pulse test, and galvanostatic intermittent titration technique (GITT) test; the low-rate test contains a constant current (CC) full charge and discharge at a very low rate, the pulse test consists of current pulses with short durations, and the GITT test is composed of a series of CC pulses at a low rate with long durations. Ref. [9] used constant current constant voltage (CCCV) charge protocol and a typical driving cycle as the test profile to simulate real-world cycles of LIBs. Generally, the total time cost of existing tests can vary from dozens of hours to a few days.

The set of parameters to be identified should be determined next because not all parameters in an electrochemical model contribute explicitly to the output and are identifiable. Ref. [10] identified solid-phase diffusion coefficients and reaction rate coefficients of the anode and cathode. Ref. [11] sorted out the identifiable parameters according to a criterion based on the Fisher information matrix. Ref. [4] investigated the freedom degree of a single particle model to...
determine the minimum set of identifiable parameters; the estimation was then conducted based on the experimental EIS data. Ref. [12] introduced a group of lumped parameters via their functional relationship with the true electrochemical parameters and then identified lumped parameters as an alternative. The similar idea was taken in ref. [13] to identify solution-phase diffusion coefficients. Ref. [14] classified parameters into three categories, thermodynamics, slow dynamics and fast dynamics, for identification. Due to the non-linearity of LIB characteristics, the observability of a certain parameter is determined by not only the system property but also the input current. Ref. [15] analyzed the parameter sensitivity of an electrochemical model under the charge process and real-world driving cycles. Ref. [9] assigned parameters to different tests with specific current profiles for identification. On the contrary, ref. [16] separated the output voltage into several components for identification.

Finally, optimal parameter values are obtained by minimizing the difference between the model prediction and the measured data in the test. Mathematically, this process is tackled by proper optimization algorithms, which are classified into two categories in existing studies, i.e., deterministic algorithms and heuristic algorithms. Due to the complexity of electrochemical models, the literature using deterministic methods is relatively limited, such as non-linear least-square [11], least-square [17], Levenberg-Marquardt algorithm [18], etc. Although deterministic algorithms usually have higher speed and lower computational cost, they are likely trapped in the local optima for complex systems. Thus, heuristic algorithms were more prevalent. Ref. [19] used the Nondominated Sorting Genetic Algorithm (NSGA) to obtain the Pareto front of parameters and selected the final identification result with the Technique for Order Preference by Similarity to Ideal Solution (TOPSIS). Ref. [20] developed the Homotopy optimization approach to identify parameters in an electrochemical model, the original differential-algebraic equations of the model are reduced to a singularly perturbed system for efficient calculation. Ref. [21] used a genetic algorithm (GA) to identify five electrochemical parameters closely related to the aging status on whole lifetime. Ref. [22] proposed a learning-based method based on deep Bayesian harmony search which is data-efficient and avoids time-consuming tests. Ref. [23] employed a particle filter to estimate a part of the parameters based on a simplified recursive aging model. Ref. [24] proposed a long short-term memory network to identify parameters in a near-optimal and real-time manner. Ref. [25] proposed a two-step parameter identification strategy based on particle swarm optimization (PSO). Variants of classic algorithms have been attempted in some studies as well, such as the multi swarm PSO (MSPSO) [5, 6].

However, for parameter identification of LIBs in real-world applications, the following requirements are still waiting to be met: i) the test time should be reduced to as short as possible, ii) only parameters that significantly affect the battery characteristics should be monitored to keep the identification framework lightweight, iii) the optimization algorithm should be improved to realize a trade-off between simplicity and accuracy so that it can be easily implemented in practice without upgrading the computing hardware. To bridge the gap, an identification framework including the test method, parameter model, and optimization algorithm, is proposed. First, various electrochemical parameters are grouped by time-variant features. A quasi-static test covering the partial SOC range is designed to identify parameters with slow dynamics at a relatively low time cost. Parameters directly related to the external characteristics are identified in a data-driven manner based on the PSO algorithm. In contrast, parameters related to the aging status are identified in a model-driven manner based on the degradation mechanisms. A dynamic test consisting of a series of CC pulses with different durations is designed to identify parameters with fast dynamics. The obtained voltage sequence is cut into segments to separate the identification of different parameters. The Sobol method is applied to conduct global sensitivity analysis and assign different parameters to specific segments for identification. A sensitivity-oriented stepwise optimization (SSO) algorithm, which decomposes the solving process into preliminary estimation and secondary identification, is designed to solve the entire identification problem with low computation cost. The quasi-static test and dynamic test are conducted independently on separated time-scales to make identification more flexible and lightweight. Contributions of this work are threefold.

- On the basis of identifiability conditions, electrochemical parameters are grouped by their variant features on the time horizon and identified in the quasi-static test or dynamic test on separated time-scales, which makes the identification flexible and lightweight for implementation.

- Slow dynamic parameters are identified in a hybrid data-driven and model-driven approach. Fast dynamic parameters are identified in different response segments according to global sensitivity analysis results. A specifically designed SSO algorithm is applied to find the proper solution efficiently with low computation costs.

- Numerical experiments on a typical NCM811 cell in different life stages are conducted for validation. It is observed that the identified parameters can not only improve the accuracy of battery model, but also be used as
indicators of the battery health status.

The rest of this paper is organized as follows: Section 2 introduces the identification approach. Section 3 presents the identification algorithm. Section 4 discusses the results of the numerical experiments. Section 5 draws conclusions.

2. Identification Approach Design

In this section, electrochemical parameters to be identified are defined first. Design of the test and identification model are presented next.

2.1. Parameter Definition

To increase the practicability of this work, we start from an interpretable and analytical electrochemical model with relatively low complexity comparing with the P2D model [26]. The mechanism and involved parameters of a typical LIB is shown in Fig. 1. Generally, electrochemical parameters can be grouped into seven categories.

The first group contains geometric parameters determined by the manufacturing, i.e., \( A_{\pm\text{sep}} \) and \( L_{\pm\text{sep}} \). The second group contains physical property parameters of active materials used in the battery, i.e., \( M \pm, \rho \pm \) and \( R \pm \). The third group contains chemical property parameters of active materials, i.e., \( k \pm \) and \( U_{\pm\text{OCP}} \). Typically, physical parameters are commonly constants e.g., \( M^- = 72.06 \text{ g/mol} \) for the Graphite electrode, while chemical parameters usually vary with the temperature or reactant concentrations, e.g., \( U_{\text{OCP}} \) (as shown in the right of Fig. 4) is a non-linear function of the Li\(^+\) concentration. The forth group contains material composition parameters determined by the manufacturing, i.e., \( \varepsilon_\pm \) and \( \varepsilon_{\pm\text{sep}} \). The fifth and sixth groups contain transport parameters in the solid-phase or solution-phase (the resistance or conductance depict the transport of electrons and the diffusion coefficients depict the transport of Li-ions). Specifically, parameters in the fifth group have scalar formats, i.e., \( R_\pm, R_e, \sigma_\pm \) and \( \mathcal{R}_\text{0} \) [27], and parameters in the sixth group have function formats, i.e., \( D_\pm, \kappa \) and \( D_e \), they are reported to be varying with the temperature or Li\(^+\) concentrations [27]. The seventh group contains macro-scope parameters, i.e., \( C_Q \) and open-circuit voltage (OCV), they are directly used in industrial applications for battery management.

For such a large number of parameters, conventional identification approaches, which optimize all parameters together to minimize the voltage error between the experiment and model, are likely to get unreasonable results as explained in the introduction. Actually, from the identification perspective, not every parameter needs to be identified. Thus, their features should be investigated first.

- Geometric parameters \( A_{\pm\text{sep}} \) and \( L_{\pm\text{sep}} \) are considered known because they can be obtained from the manufacturer and not change with the battery degradation.
Physical and chemical property parameters $M^\pm$, $\rho^\pm$, $R^\pm_r$, $k^\pm_r$ and $U^\pm_{\text{OCP}}$ reflect inherent characteristics of active materials, which remain unchanged during the degradation process. Thus, for widely studied commercial batteries, values of these parameters are available and considered known [27].

Initial values of material composition parameters $\epsilon^\pm_s$ and $\epsilon^\pm_e$ can also be obtained from the manufacturer. However, some of them will change with the battery degradation since some side reactions directly consume active materials or electrolyte. Thus, they need to be identified. Since the lifespan of commercial LIBs can commonly reach thousands of cycles, the rate of material composition loss is quite slow.

Among transport parameters, the film resistance over active particles, $R^\pm_f$, is the product of side reactions and can be treated as material composition parameters. The remainders, $R_c$, $\sigma^\pm_s$, $t_0^\pm$, $D^\pm_s$, $\kappa$ and $D_e$, are not only determined by material properties, but also affected by the composition, temperature, concentration, etc. Generally, they are more volatile than material composition parameters and need to be identified more often to keep the accuracy of the battery model.

Considering features of different parameters, the identification is decomposed into two approaches on separated time-scales from a practical point of view. Specifically, the quasi-static test is designed to identify material composition parameters without the knowledge of transport parameters. The test does not have to be conducted too often. The dynamic test is designed to identify transport parameters. The test has to be conducted more often to track dynamic characteristics of the battery. The sketch of the proposed identification framework is shown in the right of Fig. 2.

![Figure 2: The identification framework.](image)

### 2.2. Quasi-static Test

In the quasi-static test, the battery is operated under a constant current with low C-rate. Thus, the ohmic voltage drop due to the non-ideal transport of electrons in the solid-phase and solution-phase can be ignored. In addition, the migration of Li-ions in the solution-phase and diffusion of Li-ions in the solid-phase take place slowly, inducing the Li-ion concentrations along the thickness direction in the electrolyte and the radius direction in the active particles approximately uniform. Thus, the polarization potential drop due to the non-uniform distribution of Li-ions in the solid-phase and solution-phase can be ignored. Under such circumstance, we do not need to know values of transport parameters in advance and the original battery model in ref. [26] is simplified into the quasi-static form as given in Fig. 3. It is observed that only $\epsilon^\pm_s$ are directly involved in the model.

Generally, the quasi-static test is time-consuming due to the low current, e.g., it takes 100 hours to discharge the battery from full to empty when the current equals 0.01 C-rate. To save time, initial states of solid-phase Li$^+$ concentrations in active particles, denoted by $c^\pm(t_0)$, are treated as pseudo parameters to identify. Thus, the test can start and stop at any point of state of charge (SOC) as shown in Fig. 4.
Find the proper $\mathcal{E}_s$ by fitting on OCP curves

Denote the measured voltage by $\tilde{V} = [\tilde{V}(t_1), \ldots, \tilde{V}(t_N)]^\top$ and the static battery model by $f_{\text{static}}$, the optimization problem for identification is formulated as:

$$\min_{[c^\pm(t_0), c^\pm(t_1)]} \sum_{i=1}^N (\tilde{V}(t_i) - V(t_i))^2$$

subject to $[V(t_i), c^\pm(t_i)] = f_{\text{static}}(c^\pm(t_{i-1}), I, \Delta t, \mathcal{E}_s)$. \hfill (1)

After obtaining $c^\pm$ and $c^\pm(t_0)$, macro-scope characteristics of the battery, i.e., the total capacity and the OCV, can be directly derived. In real-world applications, the operating region of the battery is depicted by the voltage limitation, suggested by the manufacturer. Denote the maximum and minimum approved voltages by $V_{\text{max}}$ and $V_{\text{min}}$, the limitation of $c^\pm$ when the battery is discharged to empty, denoted by $c_{s,\text{max}}^+$ and $c_{s,\text{min}}^-$, can be solved by:

$$\begin{cases} (c_{s,\text{max}}^+ - c_{s,\text{min}}^-) \gamma = (c_s(t_0) - c_{s,\text{min}}^-) \\ U_{\text{OCP}}(c_{s,\text{max}}^+) - U_{\text{OCP}}(c_{s,\text{min}}^-) = V_{\text{min}} \end{cases} \Rightarrow \begin{cases} c_{s,\text{max}}^+ \\ c_{s,\text{min}}^- \end{cases}$$

where $\gamma = \frac{\varepsilon^+ A^+ L^+}{\varepsilon^- A^- L^-}$ is the volume ratio of positive electrode active materials to negative electrode active materials. The first equation ensures the conservation of Li-ions, and the second equation ensures voltage equality. Similarly, the limitation of $c^\pm$ when the battery is charged to full, denoted by $c_{s,\text{min}}^+$ and $c_{s,\text{max}}^-$, can be solved by replacing $c_{s,\text{max}}^+$, $c_{s,\text{min}}^-$, and $V_{\text{min}}$ in Eq. (2) with $c_{s,\text{min}}^+$, $c_{s,\text{max}}^-$, and $V_{\text{max}}$, respectively. Based on $c_{s,\text{min}}^+$, $c_{s,\text{max}}^-$, the total capacity of the battery equals the sum of the maximum capacity that can be injected and extracted at the current state as follows:

$$C_Q = (c_{s,\text{max}}^- - c_{s,\text{min}}^-) \varepsilon_s A^- L^-.$$

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For any $\text{SOC}_i \in [0, 1]$, the corresponding OCV is as follows:

$$
\text{OCV} (\text{SOC}_i) = U_{\text{OCP}}^+ (c_{s,\text{max}}^+ - \text{SOC}_i (c_{s,\text{max}}^+ - c_{s,\text{min}}^+)) - U_{\text{OCP}}^- (c_{s,\text{min}}^- + \text{SOC}_i (c_{s,\text{max}}^- - c_{s,\text{min}}^-)),
$$

(4)

Since the electrolyte volume fraction $\varepsilon_s^\pm$ and film resistance $R_f^\pm$ are not directly reflected in the voltage, empirical models derived from side reaction mechanisms are constructed to identify them. Coefficients of empirical models are fitted on results of the aging test simulated with AutoLion [27].

Generally, side reactions take place in the battery include the film growth and active particle cracking, and are more severe in the Graphite-made negative electrode than in the LiNCM-made positive electrode [28, 29]. As shown in Fig. 1, the film over NCM active particles is called cathode electrolyte interphase (CEI) and that over Graphite active particles is called solid electrolyte interphase (SEI). The CEI growth is depicted by: $\text{Li(Ni}^{3+}\text{)}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2 + 2\text{C}_2\text{H}_4\text{CO}_3 = (\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2\text{CH}_2 + 2\text{CH}_3\text{COO}_2\text{Li}$. The SEI growth is depicted by $2\text{Li} + 2\text{C}_2\text{H}_4\text{CO}_3 = (\text{CH}_2\text{OCO}_2\text{Li})_2 + \text{C}_2\text{H}_4\text{CO}_3$. Knowing the definite material composition, the electrical conductivity of the film, denoted by $\sigma_f^\pm$, are available. According to Ohm’s law, $R_f^\pm$ can be expressed by $R_f^\pm = \delta_f^\pm / \sigma_f^\pm$, i.e., knowing the film thickness $\delta_f^\pm$ is necessary.

In the NCM electrode, the CEI formation directly consumes active materials. Thus, the relationship between the increment of film thickness $\delta_f^+$ and the decrement of $\varepsilon_s^+$ is fitted by a proportional function. In the Graphite electrode, the SEI formation consumes the electrolyte. Thus, the relationship between $\delta_f^-$ increment and $\varepsilon_e^-$ decrement is fitted by a proportional function. Assume the initial thickness of SEI and CEI to be zero, we have:

$$
\delta_f^+ = k_f^+ \Delta \varepsilon_s^+, \quad \delta_f^- = k_f^- \Delta \varepsilon_e^-.
$$

(5)

where $k_f^\pm$ are fitted coefficients. For the Graphite electrode, $\varepsilon_e^-$ should be identified first. Generally, when the battery is fresh, the SEI over the active material is relatively thin, and there is abundant available surface for new SEI to grow after cracking. However, with degradation, an increasing number of surfaces have been covered by the SEI yet, and the marginal increment of the fresh surfaces decreases gradually. Thus, a parabolic function is adopted to fit the relationship between the decrements of $\varepsilon_e^-$ and $\varepsilon_s^-$ as follows:

$$
\Delta \varepsilon_e^- = k_e^- (\Delta \varepsilon_s^-)^2 + b_e^- \Delta \varepsilon_s^-.
$$

(6)

where $k_e^-$ and $b_e^-$ are fitted coefficients. According to the simulation results of AutoLion, the $\varepsilon_e^-$ almost keeps constant during the aging test. This is because the rate of CEI growth is slow and the consumption of electrolyte can be neglected. Thus, $\varepsilon_e^-$ is considered known, i.e., can be obtained from the manufacturer.

To conclude, $\varepsilon_s^\pm$, $R_f^\pm$, $\varepsilon_e^-$, $C_Q$ and OCV can be identified in the quasi-static test. These parameters are all related to the fade of material composition with slow dynamics. Thus, the test is recommended to be conducted monthly or quarterly.

### 2.3. Dynamic Test

In the dynamic test, the battery is operated in an active status so that impacts of transport parameters can be reflected in the voltage. Under such circumstance, the nonuniform distributions of Li$^+$ concentrations, reaction rates, and internal potentials and currents should be considered. Thus, the complete battery model in [26] is adopted as shown in Fig.5.

Generally, transport parameters can be categorized into two groups. As shown in Fig. 1, $\kappa$, $\sigma_s^\pm$ and $R_e$ are related to the transport of electrons, indicating their impacts might be instantly reflected in the voltage when the current suddenly changes. On the other hand, $D_s^\pm$, $D_e$ and $I_0$ are related to the transport of Li-ions, indicating their impacts might be gradually reflected in the voltage until the battery reaches a steady status after encountering current change.

Considering these properties, we use CC pulses with different durations for the test as shown in the left of Fig. 6. We can observe the voltage response typically contains four parts, i), zero-to-step instantaneous process at the start of the excitation, ii), zero-to-step transient process until the battery reaches a dynamic steady status under the galvanostatic current, iii), step-to-zero instantaneous process at the end of the excitation, iv), step-to-zero transient process until the battery reaches a static steady status under the rest. Cut points of these four parts are denoted by $N_1$, $N_2$, $N_3$ and $N$, respectively. Thus, parameters that immediately take effect can be identified in the instantaneous process, and
parameters that gradually take effect can be identified in the transient process, i.e., either the excitation period or the rest period.

There are four factors to be determined for a CC pulse, i), the duration of the excitation period, ii), the duration of the rest period, iii), the amplitude of the excitation current, iv), the battery SOC at the start of the excitation. Since the time constants of different transport parameters vary considerably, the excitation durations are set to 15/30/60/120 seconds respectively. When the excitation duration is short, only the impacts of parameters with small time constants can be fully recorded, and when the duration is long, impacts of all parameters can be recorded. Thus, parameters with different time constants can be distinguished. According to numerical experiments, it takes around 120 seconds (as shown in the right of Fig. 6) for the battery to reach a dynamic steady status under the galvanostatic current, i.e., the voltage gradually approaches a line. Thus, the maximum lasting time of the excitation is set to 120 seconds. For the rest period, the battery should have enough time to reach a static steady status. According to numerical experiments, it takes around 100 seconds (as shown in the right of Fig. 6) for the voltage to gradually converge to the constant. Thus, the duration of the rest is set to 100 seconds. Theoretically, the current amplitude and the starting SOC can also affect the voltage response. However, by numerical experiments, they are found not obviously influence the identification accuracy. Thus, without loss of generality, the current amplitude of the excitation period is set to approximately 1 C-rate, and the start SOC is set to approximately 0.6. The whole dynamic test takes approximately 10 minutes in all to conduct.

Denote the complete battery model by $f_{\text{dynamic}}$, internal states by $c\left(t_i\right)=\left[c^+_{\text{s}}\left(x,t_i\right),c^+_{\text{ss}}\left(x,t_i\right),c^+_{\text{e}}\left(x,t_i\right)\right]$, the vector of transport parameters by $\theta$ (parameters identified in the quasi-static test are considered known). Run the model in the discrete manner under the current profile, the predicted voltage sequence can be obtained:

$$V\left(t_i\right),c\left(t_i\right)=f_{\text{dynamic}}\left(c\left(t_{i-1}\right),I(t_i),\Delta t,\theta\right).$$
where $i=1,2,\ldots,N$.

For parameters that take effect instantly, they are identified by minimizing the error between $\hat{V}$ and $V$ in the instantaneous period, the objective function $f_I$ is expressed by:

$$f_I = \sum_{i=1}^{N_1} (\hat{V}(t_i) - V(t_i))^2 + \sum_{i=N_2}^{N_3} (\hat{V}(t_i) - V(t_i))^2. \quad (8)$$

Similarly, for parameters that take effect gradually, they are either identified in the excitation period or rest period, the objective functions $f_E$ and $f_R$ are expressed by:

$$f_E = \sum_{i=N_1}^{N_2} ((\hat{V}(t_i) - \hat{V}(t_{N_1})) - (V(t_i) - V(t_{N_1})))^2. \quad (9)$$

$$f_R = \sum_{i=N_3}^{N} ((\hat{V}(t_i) - \hat{V}(t_{N_3})) - (V(t_i) - V(t_{N_3})))^2. \quad (10)$$

The bias originating from the instantaneous period is eliminated in the formula of $f_E$ or $f_R$. However, the optimization problem is still intractable, e.g., when identifying parameters that take effect instantly, parameters that take effect gradually also need to be known to calculate Eq.(7). Actually, they are unknown. Thus, specific algorithm needs to be developed to tackle the problem.

Last, note that $D^{\pm}$, $D_e$ and $\kappa$ have function formats as mentioned in Section 2.1. Directly identifying their expressions is intractable. Thus, accommodation factors are introduced to transform them into scalar formats, e.g., $\kappa = \hat{\kappa} f_\kappa$, where $f_\kappa$ is the original expression and $\hat{\kappa}$ is the accommodation factor. While retaining the basic material properties, the volatility of $\kappa$ can be reflected in $\hat{\kappa}$. Thus, identifying $\kappa$ is replaced by identifying $\hat{\kappa}$. For notation simplicity, ($\cdot$) and ($\hat{\cdot}$) are not distinguished in the following text.

3. Identification Algorithm Design

In this section, specific identification algorithms for the quasi-static test and the dynamic test are designed.

3.1. Classic heuristic optimization

In the quasi-static test, $\epsilon^{\pm_1}$ and $c^{\pm_1}(t_0)$ are obtained by optimizing Eq.(1). As shown in Fig. 3, $U_{OCP}^{\pm}$ are nonlinear, indicating that deterministic optimization algorithms are likely trapped in a local minimum when encountering incorrect initialization. Based on the fact that the static battery model is simple and the voltage sequence length is short (because the sampling frequency is low), classic heuristic optimization algorithms, i.e., PSO or GA, are applied. The basic idea of these two algorithms is searching for the optimum via the competition and cooperation of populations. In practice, they can be conveniently called on different computation platforms, e.g., MATLAB and Python. For details of these two algorithms, refer to [30, 31].

3.2. Sensitivity-oriented stepwise optimization

In the dynamic test, the identification is more complex since all parameters are activated and their effects on the voltage are mixed up. Directly identifying them together may get unreasonable results for such an ill-conditioned problem. Thus, an SSO algorithm is designed, which contains three steps, i), calculating the sensitivity of different parameters to the voltage in different periods, ii), identifying parameters sensitive to the voltage in the instantaneous period in a stepwise manner, iii), identifying parameters sensitive to the voltage in the transient process, either the excitation period or rest period, in a stepwise manner.

3.2.1. Sensitivity analysis

Under the dynamic status, the battery is a typical non-additive and nonlinear system, i.e., the model output is attributed not only to different parameters separately but also to their interactions. Thus, the commonly used simple sensitivity analysis frameworks, such as variance calculation [9] or one-at-a-time [15], can hardly give reliable results.
To solve this problem, a widely used global sensitivity analysis framework, i.e., the Sobol method, is applied [32]. The Sobol method works within a probabilistic framework and is suitable to multi-parameter systems.

Since the Sobol method requires the scalar input, objective functions \( f_I, f_E \) and \( f_R \) are applied to transform the voltage sequence into scalars. Take the sensitivity of the \( k \)-th parameter in \( \theta \) to the voltage in the instantaneous process as an example. Introduce two random variables first, \( \Theta_k \) means only the \( k \)-th element in \( \theta \) is random and \( \Theta_{-k} \) means all elements except the \( k \)-th element in \( \theta \) is random. Denote the random variable of \( f_I \) by \( F_I \), the Sobol sensitivity is calculated by:

\[
s_k = \frac{\mathbb{E}_{\Theta_{-k}} \left( \text{Var}_{\Theta_k} (F_I | \Theta_{-k}) \right)}{\text{Var}(F_I)}.
\]

Mathematically, \( s_k \) represents the fraction of the total output variance that would remain on average as long as the \( k \)-th parameter stays unknown. A higher \( s_k \) indicates that the \( k \)-th parameter is more sensitive to the voltage. For a complex system, calculating Eq. (11) by analytical integrals is intractable. The Sobol method gives a numeric way to estimate \( s_k \) based on Monte Carlo integrals. When the sampling scale increases, the Monte Carlo results gradually converge to the analytical results. According to existing research, replacing conventional random sequences with quasi-random low-discrepancy sequences such as the Sobol sequence can further improve the convergence rate [33], which is adopted in this work. For details of generating the Sobol random numbers, refer to [34].

After generating \( 2M \) samples of parameter vectors by the quasi-Monte Carlo sequence, compact them to matrix form:

\[
\begin{bmatrix}
\theta_1^T \\
\theta_2^T \\
\vdots \\
\theta_{2M}^T
\end{bmatrix}
= 
\begin{bmatrix}
\theta_{1,1} & \theta_{1,2} & \cdots & \theta_{1,p} \\
\theta_{2,1} & \theta_{2,2} & \cdots & \theta_{2,p} \\
\vdots & \vdots & \ddots & \vdots \\
\theta_{2M,1} & \theta_{2M,2} & \cdots & \theta_{2M,p}
\end{bmatrix}_M 
\]

(12)

where \( p=8 \) is the number of parameters. Every row of \( \Xi \) corresponds to a parameter vector sample. Substituting the \( j \)-th row into Eq. (7) and calculating \( f_I \) via Eq.(8), denoted by \( f_{I,j} \). The denominator of Eq. (11) can be estimated by:

\[
\text{Var}(F_I) \approx \frac{1}{2M - 1} \sum_{j=1}^{2M} (f_{I,j} - \bar{f}_I)^2. 
\]

(13)

where \( \bar{f}_I \) equals the mean value of \( f_{I,j} \).

To calculate the numerator of (11) for the \( k \)-th parameter, we construct a new \( M \times p \) matrix \( \Xi^k \) based on \( \Xi \):

\[
\begin{bmatrix}
\theta_1^k^T \\
\theta_2^k^T \\
\vdots \\
\theta_{M}^k^T
\end{bmatrix}
= 
\begin{bmatrix}
\theta_{1,1} & \cdots & \theta_{M+1,k} & \cdots & \theta_{1,p} \\
\theta_{2,1} & \cdots & \theta_{M+2,k} & \cdots & \theta_{2,p} \\
\vdots & \ddots & \vdots & \ddots & \vdots \\
\theta_{M,1} & \cdots & \theta_{M,k} & \cdots & \theta_{M,p}
\end{bmatrix}_M 
\]

(14)

Specifically, the \( k \)-th elements of the 1-st to \( M \)-th rows of \( \Xi \) are replaced by the \( k \)-th elements of the \((M+1)\)-th to \( 2M \)-th rows of \( \Xi \). Substitute the \( j \)-th row into Eq. (7) and calculating \( f_I \) via Eq. (8), denoted by \( f_{I,j}^k \). The numerator of Eq. (11) can be estimated as follows:

\[
\mathbb{E}_{\Theta_{-k}} \left( \text{Var}_{\Theta_k} (F_I | \Theta_{-k}) \right) \approx \frac{1}{2M} \sum_{j=1}^{M} \left( f_{I,j} - f_{I,j}^k \right)^2.
\]

(15)

Similarly, the sensitivity of parameters to the voltage in the excitation period and rest period can be calculated by replacing \( f_I \) with \( f_E \) or \( f_R \) in the above steps.

In the dynamic test, four voltage sequences are obtained in all, denote the instantaneous periods by \( \xi_1 \sim \xi_4 \), the excitation periods by \( \xi_5 \sim \xi_8 \) and the rest periods by \( \xi_9 \sim \xi_{12} \). The Sobol sensitivity of every parameter to the voltage...
in every period can be expressed by an 8×12 matrix $S$ as shown in Fig. 7. Calculate the mean sensitivity of every parameter in instantaneous periods, excitation periods and rest periods, denoted by $\hat{s}_k^1, \hat{s}_k^2$ and $\hat{s}_k^R$, respectively. For $\theta_k$, if $\hat{s}_k^1$ is the maximum, it will be identified in the instantaneous process; otherwise, it will be identified in the transient process, either the excitation period or rest period. The sets of parameters to be identified in instantaneous process and transient process are denoted by $\Theta^I$ and $\Theta^T$, respectively.

3.2.2. Stepwise optimization

Considering the measurement precision of existing voltage sensors, parameters with the Sobol sensitivity below 0.01 are removed from the identification task and directly set to empirical values. Parameters in $\Theta^I$ are identified first because the effects of parameters in $\Theta^T$ have not yet been reflected in the voltage.

Denoting the size of $\Theta^I$ by $N_I$ and resorting its elements by $\hat{s}_k^1$ in descending order, we have $\Theta^I=\{\theta_1^I, \theta_2^I, \ldots, \theta_{N_I}^I\}$.

First, the preliminary estimation is conducted one by one from $\theta_1^I$ to $\theta_{N_I}^I$. Taking $\theta_1^I$ as an example, locate the period $\zeta_j$ where it has the highest sensitivity, i.e., $j=\arg\max_{1 \leq j \leq 4} S^I_{1,j}$. The preliminary estimation, denoted by $\hat{\theta}_1^I$, is obtained by minimizing $f_1$ in $\zeta_j$. Since other parameters are unknown, they are set to random values between reasonable ranges. The adopted optimization algorithm can be either deterministic algorithms, i.e., the active set method, or the heuristic algorithms, i.e., PSO or GA. The selection of the algorithm is determined by the effect of $\theta_1^I$ on the voltage. Specifically, if the relationship between $\theta_1^I$ and $f_j$ approximately follows a convex trajectory, the risk of being trapped in a local minimum can be avoided. Then, an exact algorithm with high speed is selected. Otherwise, a heuristic algorithm that can provide a relatively global optima is selected. Since the battery model is complex, explicitly analyzing the convexity is difficult, and the specific algorithm is determined according to the results of numerical experiments in this work. For the following parameters, repeat the steps above. The main difference is that when estimating the $i$-th parameter $\theta_i^I$, set $\theta_j^I, j<\theta_i^I$ to $\bar{\theta}_j^I$, and the remaining parameters to random values. After the loop finishes, we can obtain $\{\bar{\theta}_1^I, \bar{\theta}_2^I, \ldots, \bar{\theta}_{N_I}^I\}$.

Next, the voltage piece $\zeta_j$ is located by $j=\arg\min_{1 \leq j \leq 4} \left(\max(s_m^j) - \min(s_n^j)\right)$ for $j=1, 2, 3, 4$, and $m, n=1, 2, \ldots, N_I$, i.e., the difference between the highest sensitivity and the lowest sensitivity is the smallest. This ensures the weights of all parameters are relatively equal. The final identification is obtained by optimizing $f_j$ in $\zeta_j$. Since all parameters are involved, the heuristic algorithm is adopted to search for the global optimum. The lower and the upper bounds of optimization variables are set as 95% and 105% of the preliminary estimation values, i.e., $0.95 \theta_j^I \leq \hat{\theta}_{j}^I \leq 1.05 \theta_j^I$, $j=1, 2, \ldots, N_I$, which ensures that the identification of parameters with low sensitivity is not being affected by other parameters considerably. Denote the identified result by $\{\hat{\theta}_1^I, \hat{\theta}_2^I, \ldots, \hat{\theta}_{N_I}^I\}$.

Parameters in $\Theta^T$ are identified similarly. First, sort the parameters according to their sensitivity in descending order. Second, locate the proper period to estimate every parameter preliminarily one by one. Finally, locate the proper period to estimate all parameters together based on preliminary estimations. The sketch of the SSO algorithm is given in Fig. 7.

4. Experimental Results

The performance of identification on a typical NCM811 18650 battery cell with a capacity of 2200 mAh is studied. The fresh battery is alternately discharged and charged in a 1 C-rate galvanostatic current for 2000 full cycles. The identification is conducted for the battery after 0/500/1000/1500/2000 degradation cycles to validate the adaptability of this work to batteries at different life stages. Note that many parameters to be identified are immeasurable for real batteries. For ease of evaluation, the experiment is conducted by AutoLion, which is a state-of-the-art commercial software that is widely used in academia and industry for lithium-ion battery studies [27]. Parameters of the battery for simulation are set to default values of the software, which can also be inquired in [28]. Since the parameters to be identified are all scalars, we use the mean absolute error (MAE) as the accuracy metric as follows: $\text{MAE}=|\hat{\theta} - \theta|/\theta$.

4.1. Quasi-static test result

The galvanostatic current of the quasi-static test is set to 0.01C-rate, i.e., 22mA. Since the voltage decreases very slow under the low current, the sampling interval is set to 200s. To locate the proper SOC interval, we conduct the test starting at different SOCs with different durations. The identification errors of $\varepsilon_{s}^{-}$ of the battery at the fresh state and the aged state (2000 cycles) are plotted in Fig. 8. It is observed that starting at lower SOCs with longer durations
Figure 7: Sensitivity-oriented stepwise optimization.

Figure 8: Identification error of $\varepsilon_i$ under different settings of the quasi-static test.

generally leads to higher accuracy. This finding is reasonable because the gradient of OCV is higher at lower SOCs, which makes the observation easier, as shown in Fig. 4. Specifically, we find that starting around SOC= 0.6 with the duration of 20000 s (i.e., N= 100) is relatively more accurate than other cases. Since the Li$^+$ stoichiometry range in active materials is unknown, the SOC cannot be defined accurately. Thus, the OCV is used as an indicator to replace the SOC, i.e., the quasi-static test is recommended to start at OCV= 3.8 V (roughly near SOC= 0.6) and lasts for 20000 s until 100 measurement points are obtained.

The PSO is applied to identify $\varepsilon_i(t_0)$ and $\varepsilon_i^\pm$. The swarm size is set as 200, the function tolerance is set as $10^{-6}$, and the lower and upper boundaries of the optimized variables are 80% and 120% of the true values, respectively. The experimental results indicate that the average optimization time is approximately 3 seconds. The identification accuracy of cells at different life stages is given in Table 1. For every parameter, the first row in bold font is the...
Table 1
The identification results of $\theta_s^-(t_0)$ and $\varepsilon_s^\pm$.

| cycles | 0    | 500  | 1000 | 1500 | 2000 |
|--------|------|------|------|------|------|
| $\theta_s^-(t_0)$ | 0.487 | 0.483 | 0.480 | 0.478 | 0.477 |
| $\theta_s^+(t_0)$ | 0.536 | 0.535 | 0.534 | 0.533 | 0.532 |
| $\varepsilon_s^-$ | 0.099\% | 0.097\% | 0.088\% | 0.089\% | 0.089\% |
| $\varepsilon_s^+$ | 0.536 | 0.535 | 0.534 | 0.533 | 0.532 |
| $\varepsilon_s^-$ | 0.023\% | 0.005\% | 0.001\% | 0.008\% | 0.015\% |
| $\varepsilon_s^+$ | 0.666 | 0.654 | 0.643 | 0.633 | 0.624 |
| $\varepsilon_s^-$ | 0.142\% | 0.121\% | 0.332\% | 0.203\% | 0.089\% |
| $\varepsilon_s^+$ | 0.520 | 0.517 | 0.516 | 0.515 | 0.514 |

Identified value, the second row is the true value and the third row is the error metrics. Note that the GA can also achieve similar performance in terms of accuracy and speed, which is omitted in the text due to limited space. It is observed that all four parameters can be accurately and efficiently identified. Based on them, $C_Q$ and OCV curve can be derived, as shown in Fig. 9. Although the identification error increases gradually with degradation, its absolute value generally meets the requirement, i.e., smaller than 0.5%.

![SOC-OCV curve](image1.png)

(a) SOC-OCV curve.

![Total capacity](image2.png)

(b) Total capacity.

**Figure 9:** Identification results of macro-scope characteristics of the NCM811 battery

The remaining parameters, $\varepsilon_e^-$ and $R_f^\pm$, are identified via empirical models. Coefficients in Eq. (5)-(6) are fitted on five randomly selected cycles and listed in Table 2. The identification result is presented in Table 3. It can be observed that $\varepsilon_e^-$ can be identified accurately for the battery under different life stages. Since the initial thickness of SEI/CEI film is assumed to be zero, the identification error of $R_f^\pm$ is quite high in the early life stage. However, the accuracy gradually increases with the battery degradation. As important indicators of the battery health, it is more meaningful to identify $R_f^\pm$ for aged batteries. Thus, a relatively large error in the early life stage is acceptable.
Table 2
The fitted coefficients in empirical models.

| Fitted Coefficients | $k^+_f$ (nm) | $k^-_f$ (nm) | $k^-_e$ | $b^-_e$ | $\sigma^+_f,0$ (S/m) | $\sigma^-_f,0$ (S/m) |
|---------------------|--------------|--------------|---------|---------|----------------------|----------------------|
|                     | -7.68e3      | -3.76e3      | 6.00    | 0.659   | 1.52e-5              | 1.54e-5              |

Table 3
The identification results of $\varepsilon^-_e$ and $R^-_f$.

| cycles | 0      | 500    | 1000   | 1500   | 2000    |
|--------|--------|--------|--------|--------|---------|
| $\varepsilon^-_e$ | 0.2833 | 0.2763 | 0.2710 | 0.2679 | 0.2658  |
|                | 0.2827 | 0.2762 | 0.2720 | 0.2686 | 0.2656  |
|                | 0.22%  | 0.02%  | 0.36%  | 0.26%  | 0.04%   |
| $R^-_f$ ($10^{-4}$Ωm²) | 3.34  | 19.26  | 29.80  | 38.28  | 45.56   |
|                | 0%     | 10.1%  | 2.07%  | 0.09%  | 4.56%   |

| cycles | 0      | 500    | 1000   | 1500   | 2000    |
|--------|--------|--------|--------|--------|---------|
| $R^-_f$ ($10^{-4}$Ωm²) | 1.46  | 15.45  | 21.86  | 26.78  | 30.93   |
|                | 100%   | 14.3%  | 3.96%  | 0.94%  | 0.95%   |

Table 4
The sampling range of transport parameters.

| params | true value | sampling range     | params | true value | sampling range     |
|--------|------------|--------------------|--------|------------|--------------------|
| $R_c$  | 6.4e-3     | [0, 0.05]          | $\sigma^-_s$ | 66.5       | [6.6, 100]         |
| $D^+_s$ | 1           | [0.1, 1.5]         | $t^+_c$ | 0.38       | [0.2, 0.45]        |
| $\sigma^+_s$ | 1.97       | [0.2, 3]           | $\kappa$ | 1          | [0.1, 1.5]        |
| $D^-_s$ | 1           | [0.1, 1.5]         | $D_e$  | 1          | [0.1, 1.5]         |

4.2. Sensitivity analysis

Reasonable ranges of parameters to be identified in the dynamic test are set broadly to obtain a comprehensive result, as shown in Table 4. Note also that the ranges are asymmetric around the true values because during battery degradation, the conductivity or diffusion parameters gradually decrease while the resistance gradually increases. Thus, the range is extended in the direction of the parameter evolution during battery degradation.

To obtain reliable results, a proper sampling scale $M$ should be determined first. Take the current profile with 120 seconds excitation as an example, the sensitivity of parameters in the excitation period when $M=100, 500, 1000, 1500, 2000$ is plotted in the left of Fig. 10. It is observed that when $M$ exceeds 1000, the Sobol sensitivity tends to reach convergence. To realize a trade-off between reliability and cost, $M$ is set to 1000 in this work. In contrast to a prevalent density-based method, PAWN [35], the Sobol method also performs well as shown in the right of Fig. 10. In different periods, the rankings of the first three parameters with high sensitivity are the same by two methods. However, results of the Sobol method are easier for us to distinguish between different parameters, e.g., in the instantaneous period, $R_c$ and $\kappa$ can be explicitly distinguished from the remaining parameters. Meanwhile, the Sobol method directly uses objective functions as the input, which ensures consistency between sensitivity analysis and the subsequent optimization. Thus, the Sobol method is adopted to assign parameters to $\Theta^I$ and $\Theta^T$ for identification, the results are shown in Fig. 11.

Generally, transport parameters can be divided into three groups. The first group contains $\sigma^+_s$ and $D^-_s$, which have little impact on the voltage in every period (the Sobol sensitivity is smaller than 0.01). The low sensitivity of $\sigma^+_s$ is because active materials are commonly mixed up with conductive filler additives and can be viewed as good...
conductors, inducing the ohmic potential drop in the solid-phase negligible in the voltage. The low sensitivity of $D_s^-$ is attributed to the small gradient of $U^{-}_{OCP}$ (as shown in Fig. 4). Specifically, $D_s^-$ controls the diffusion process of Li-ions in active particles and determines Li-ion concentrations on the surface of active particles, denoted by $c_{ss}$, which appears explicitly in the voltage as a term of $U^{-}_{OCP}(c_{ss})$ [26]. When the gradient of $U^{-}_{OCP}$ is very small, the change in $c_{ss}$ can hardly be observed from the voltage. With such low sensitivity, the identification results are likely to be unreliable. Thus, $\sigma_s^\pm$ and $D_s^-$ are dropped and set to empirical values.

The second group, i.e., $\Theta^I$, contains $R_c$ and $\kappa$. They are sensitive to the instantaneous process because the transport of electrons is fast and can be quickly reflected in the voltage when the current changes. The third group, i.e., $\Theta^I$, contains $D_s^+, t_0^+$ and $D_e$. They are sensitive to the transient process. This is because $D_s^+$ dominates the diffusion process of Li$^+$ in active materials of the positive electrode, $t_0^+$ and $D_e$ dominate the migration process of Li$^+$ in the electrolyte. Different from electrons, the transport of Li-ions needs time to take place, their impacts on the voltage are usually gradually reflected in the voltage. Thus, the sensitivity analysis results are consistent with physical interpretations.

Figure 11: The Sobol sensitivity of parameters to the voltage in different periods when $M=1000$. 

| Parameter | 15s-E | 30s-E | 60s-E | 120s-E | 15s-R | 30s-R | 60s-R | 120s-R | 15s-I | 30s-I | 60s-I | 120s-I |
|-----------|-------|-------|-------|--------|-------|-------|-------|--------|-------|-------|-------|--------|
| $R_c$     | 3.86E-28 | 8.46E-29 | 2.95E-29 | 1.01E-29 | 0   | 0   | 0   | 0   | 0.104 | 0.103 | 0.102 | 0.101 |
| $D_s^+$   | 0.0482 | 0.119 | 0.261 | 0.400 | 0.674 | 0.415 | 0.190 | 0.124 | 5.98E-06 | 1.09E-05 | 1.16E-05 | 1.60E-06 |
| $\sigma_s^+$ | 4.85E-05 | 2.42E-05 | 1.47E-05 | 6.04E-06 | 5.05E-05 | 2.40E-05 | 2.44E-05 | 5.82E-06 | 0.00193 | 0.00192 | 0.00203 | 0.00181 |
| $D_s^-$   | 9.77E-05 | 0.0004 | 0.0015 | 0.0012 | 0.0045 | 0.0044 | 0.00238 | 0.00597 | 1.67E-08 | 7.14E-08 | 7.76E-07 | 3.44E-06 |
| $\sigma_s^-$ | 3.76E-06 | 1.59E-06 | 4.58E-07 | 9.26E-08 | 7.76E-06 | 4.20E-06 | 9.40E-07 | 1.94E-07 | 2.52E-06 | 2.53E-06 | 2.44E-06 | 2.49E-06 |
| $t_0^+$   | 0.803  | 0.613 | 0.399 | 0.247 | 0.782 | 0.650 | 0.492 | 0.440 | 4.71E-05 | 9.01E-05 | 0.000156 | 0.000191 |
| $\kappa$  | 0.005  | 0.002 | 0.0008 | 0.0004 | 0.0096 | 0.0066 | 0.00135 | 0.000570 | 0.0106 | 0.0106 | 0.0105 | 0.0103 |
| $D_e$     | 0.130  | 0.221 | 0.3094 | 0.309 | 0.082 | 0.219 | 0.341 | 0.464 | 4.81E-06 | 1.56E-07 | 1.89E-05 | 9.20E-05 |
Table 5  
The identification results of transport parameters.

| cycles  | 0      | 500    | 1000   | 1500   | 2000   |
|---------|--------|--------|--------|--------|--------|
| $R_c \left(10^{-3}\Omega m^2\right)$ | 8.58   | 8.26   | 7.45   | 6.88   | 6.91   |
|         | 34.1\% | 29.1\% | 16.4\% | 7.50\% | 7.97\% |
| $\kappa$ | 0.997  | 1.041  | 1.052  | 0.988  | 1.002  |
|         | 0.3\%  | 4.1\%  | 5.2\%  | 1.2\%  | 0.2\%  |
| $D^+_s$ | 1.416  | 1.384  | 1.376  | 1.386  | 1.390  |
|         | 41.6\% | 38.4\% | 37.6\% | 38.6\% | 39.0\% |
| $t_0^+$  | 0.373  | 0.384  | 0.370  | 0.365  | 0.368  |
|         | 1.84\% | 1.05\% | 2.63\% | 3.95\% | 3.16\% |
| $D_e$    | 1.296  | 1.254  | 1.283  | 1.283  | 1.273  |
|         | 29.6\% | 25.4\% | 28.3\% | 28.3\% | 27.3\% |
| Run time(s) | 414   | 422    | 427    | 418    | 439    |

4.3. Dynamic test result

For clarity, the period that a certain parameter has the highest sensitivity is painted green and the period that parameters in the same set have the smallest sensitivity difference is painted red in Fig. 11. According to the SSO algorithm, the solving process contains seven steps in all, i), $R_c$ is preliminarily estimated in 15s-I period, ii), the preliminary guess of $\kappa$ is preliminarily estimated in 30s-I period, iii), final values of $R_c$ and $\kappa$ are identified in 30s-I period, iv), $t_0^+$ is preliminarily estimated in 15s-E period, v), $D^+_s$ is preliminarily estimated in 15s-R period, vi), $D_e$ is preliminarily estimated in 120s-R period, vii), final values of $D^+_s$, $t_0^+$ and $D_e$ are identified in 60s-E period. It should be noted that 15s-I is the abbreviation of the instantaneous period under the current profile with 15 seconds excitation. By numerical experiments, the proper solver and the specific setting are determined for each step as shown in Fig. 12. Take the identification of fresh battery as an example, the computation time in each step is given in the box between adjacent nodes. It is observed that the cooperation of solvers can reduce the computation time by approximately half comparing with direct optimization.

The identification results under different life stages are presented in Table 5, where the first row of each parameter refers to the identified value and the second row refers to the MAE (the true values are listed in Table 4). It is observed that the MAEs of $R_c$, $D^+_s$ and $D_e$ are relatively large. This originates in the inherent error of the simplified model in [26]. Specifically, the identification results of $R_c$, $D^+_s$ and $D_e$ are impacted by the reaction rate distribution approximation, solid-phase diffusion approximation and solution-phase migration approximation, respectively. Since the identification aims to minimize the voltage error, it can lead to biases in these parameters. As shown in Table 6, we can see that the voltage prediction errors are at least reduced by half comparing with using the true parameters. Thus, the biases in the identified values of $R_c$, $D^+_s$ and $D_e$ are reasonable and necessary; they can actually be viewed as a patch of the original model. In addition, it is observed that the bias of $R_c$ decreases roughly with battery degradation, indicating it can also be treated as an indicator of the battery health status.
Table 6
The voltage prediction RMSE ($\times10^{-3}$V).

| cycles | 0  | 500 | 1000 | 1500 | 2000 |
|--------|----|-----|------|------|------|
| Excitation lasts 15s | 2.4 | 3.9 | 4.8 | 5.7 | 6.5 |
| Excitation lasts 30s | 3.2 | 4.7 | 6.0 | 7.1 | 8.1 |
| Excitation lasts 60s | 3.9 | 5.0 | 6.4 | 7.1 | 8.0 |
| Excitation lasts 120s | 4.1 | 4.2 | 5.8 | 7.5 | 9.1 |

The SSO algorithm is also compared against the classic PSO and GA, as shown in Fig. 13. It can be observed that the computation time can be reduced by approximately half to search for an acceptable solution, which can efficiently reduce the burden of practical implementation. After all the parameters are identified, two typical current profiles are selected to validate the model, as shown in Fig. 14. One is a full-cycle discharge scenario that contains not only galvanostatic step signals but also impulse signals, and the other is a typical scenario in which the battery provides regulation service, the regulation signal is from real data in the Pennsylvania-New Jersey-Maryland (PJM) electricity market. In both scenarios, the model exhibits high accuracy after parameterization.

Figure 13: Comparison between SSO, PSO and GA.

5. Conclusion

An efficient and lightweight parameter identification framework on separated time-scales, including the test, model, and algorithm, is proposed. A few microscopic or macroscopic parameters with physical interpretations are identified accurately and efficiently for batteries at different aging stages. After the parameterization, the battery model performs better on typical working profiles. In addition, the identified parameters can be utilized as the indicator of the battery’s health status. However, there also remain some drawbacks in this work. First, considering the limitation of recent
measuring technology, only the current and voltage are utilized for identification, which restricts the scope of identified parameters. With the deployment of advanced sensors, the identification method needs to be improved. Thus, some parameters with low sensitivity to the voltage can be observed. Second, the SSO is developed at the sacrifice of accuracy to save the computational cost. It would be better if the accuracy could be reduced furthermore. We will focus on the problems above and improve the identification method in the future work.

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