Automatic Estimation of Parameters of a Reduced Order Electrochemical Model for Lithium-ion Batteries at the Beginning-of-life

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***Abstract*—This paper presents a procedure for automatic estimation of parameters of a lithium-ion battery at the beginning-of-life. Based on a reduced order electrochemical model, a two-step sensitivity analysis is employed to group the parameters and divide them using the best state-of-charge (SOC) window. Then, a genetic algorithm is applied to minimize a multi-objective function that is the L^2 norm of the voltage error for each SOC window. Results of the procedure are validated against a multiple cycle and an actual driving cycle test, which keep the absolute voltage errors less than 12mV.**

Keywords—automatic parameter estimation, genetic algorithm, lithium-ion battery, reduced order electrochemical model

I. INTRODUCTION

In recent years, lithium-ion batteries (LIBs) have been widely used as rechargeable energy storage for hybrid electric vehicles, plug-in hybrid electric vehicles, and electric vehicles [1]. LIBs have become one of the most desirable and promising energy storage devices because of their high power and high energy density as well as their low self-discharging rate.

To ensure reliable and safe operations, a battery management system (BMS) is required [2], which is designed based on battery models such as equivalent circuit models (ECMs) and physics-based models. The ECMs are widely used by industries because of their simplicity in characterization, parameter estimation, and implementation in BMS hardware. However, these types of models lack the ability of long-term prediction. In addition, the circuit elements used to construct the model do not adequately represent the physical behaviors of the internal processes of a battery. Conversely, physics-based models that are based on electrochemical principles take into account transportations of ions and charges as well as material properties. One of the frequently referenced physics-based models is Doyle-Fuller-Newman (DFN) model [3]. The model is based on the concentrated solution and the porous electrode theory coupled with the electrochemical kinetics. The governing equations are formulated by a set of coupled partial differential equations (PDEs) and are therefore computationally expensive. To reduce the computational costs, a reduced order model (ROM) has been developed under the framework of DFN model. In Table I, the governing equations of the DFN model and the associated order reduction techniques are listed. Padé approximation and the residual grouping (RG) method are used to simplify the equation of ion concentration in electrodes and electrolyte, respectively. In addition, proper orthogonal decomposition (POD) method is employed to reduce the order of governing equations for potentials in electrodes and electrolytes. Moreover, the Bulter-Volmer (BV) equation is linearized using the Taylor series expansion. Detailed descriptions of the reduction methods can be found in our previous work [4], [5].

At the beginning-of-life (BOL), the developed ROM has 20 parameters that are listed in Table II. The values of parameters are obtained from the manufacturer, literature or measurements. However, the parameters such as diffusion coefficients vary under different operating conditions and are therefore hard to measure unless doing postmortem analyses. Otherwise, the parameters can be found by manual tuning, which is time-consuming and difficult to find the optimal values. Therefore, it is imperative to develop an automatic procedure that can efficiently find a set of optimal parameters.

A number of recent studies have addressed the parameter estimation (PE) methods. Santhanagopalan et al. proposed a PE method for a ROM based on a least-square framework using Lavenberg-Marquardt (LM) method, which was validated against the experimental data up to 2C [6]. However, with inappropriate parameter initialization, the LM method may drive the objective function to a local minimum, which ends up with false optimal values. To resolve the problem of local optimum entrapment, Forman et al. used a genetic algorithm (GA) to find the values of 88 parameters extracted from a DFN model [7]. The parameters were estimated using two driving cycles and then validated using another five driving cycles. Simulations showed a good match with the experimental data, but only at low C-rate discharge (≤1C). In addition, it took three weeks to complete calculation of the parameter set on a cluster of computers without grouping or ranking the parameters. Jokar et al. proposed another PE method using the GA that considered

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TABLE I. GOVERNING EQUATIONS FOR FOM AND ORDER REDUCTION TECHNIQUES FOR ROM

	DFN model	ROM
Ion concentration in electrode particles	$\frac{\partial C_s}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_s}{\partial r}\right)$ $\left.\frac{\partial C_s}{\partial r}\right\|_{r=0} = 0$ $D_s\left.\frac{\partial C_s}{\partial r}\right\|_{r=R_s} = -\frac{j^{Li}}{a_s F}$ B. C. [a]	Padé approximation
Ion concentration in electrolyte	$\frac{\partial(\varepsilon_e C_e)}{\partial t} = \frac{\partial}{\partial x}\left(D_e^{eff}\frac{\partial}{\partial x}C_e\right) + \frac{1-t_+^0}{F}j^{Li}$ $\left.\frac{\partial C_e}{\partial x}\right\|_{x=0} = \left.\frac{\partial C_e}{\partial x}\right\|_{x=L} = 0$ B. C.	Residue Grouping
Potential in electrode	$\frac{\partial}{\partial x}\left(\sigma^{eff}\frac{\partial}{\partial x}\phi_s\right) - j^{Li} = 0$ B. C. $-\sigma_-^{eff}\left.\frac{\partial \phi_s}{\partial x}\right\|_{x=0} = -\sigma_+^{eff}\left.\frac{\partial \phi_s}{\partial x}\right\|_{x=L} = \frac{I}{A}$ $\left.\frac{\partial \phi_s}{\partial x}\right\|_{x=L_-} = \left.\frac{\partial \phi_s}{\partial x}\right\|_{x=L_-+L_{sep}} = 0$	POD
Potential in electrolyte	$\frac{\partial}{\partial x}\left(\kappa^{eff}\frac{\partial}{\partial x}\varphi_e\right) + \frac{\partial}{\partial x}\left(\kappa_D^{eff}\frac{\partial}{\partial x}\ln C_e\right) + j^{Li} = 0$ $\left.\frac{\partial \phi_e}{\partial x}\right\|_{x=0} = \left.\frac{\partial \phi_e}{\partial x}\right\|_{x=L} = 0$ B. C	
Electrochemical Kinetics	$j^{Li} = a_s i_0\left\{\exp\left[\frac{\alpha_a F}{RT}\eta\right] - \exp\left[-\frac{\alpha_c F}{RT}\eta\right]\right\}$ Activation overpotential $\eta = \phi_s - \phi_e - U_{equi}$	Linearization

[a.] Boundary condition.

both low (≤1C) and high (>1C) C-rates discharge. Based on a simplified DFN model, the model parameters were separated and optimized by time intervals obtained from sensitivity analyses of discharge characteristics [8]. The proposed method was tested with batteries with different electrode materials like $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$ [9]. However, the parameters estimated using discharge characteristics may not be appropriate for validations of charging or driving cycles. A similar heuristic computation method, particle swarm optimization (PSO), was employed to estimate four parameters of a $LiCoO_2$ battery [10], where the fitness function reached the minimum value within 100 iterations. However, the fast convergence was achieved by setting the initial values of estimated parameters as obtained from literature.

The studies mentioned above reveal that LM as a gradient-based algorithm allows for a fast convergence but does not guarantee the global minimum. Conversely, gradient-free algorithms such as the GA and the PSO, allow for convergence of a global minimum but consume a relatively considerable amount of time. In this paper, we proposed an automatic PE procedure for a lithium-ion battery at the BOL. The procedure enables one to find a set of parameters without conducting postmortem analysis, regardless of formats or designs, and without putting a vast effort by manual tuning. The PE procedure consists of a grouping of parameters, defining of objective functions and optimization. The grouping is carried out based on two criteria, sensitivity of the parameters under influences of

TABLE II. SOURCES OF PARAMETERS AT THE BOL

Source	Parameter	Symbol	Unit
Manufacturer	Electrode plate area	A	cm^2
	Thickness	δ	cm
	Particle radius	R_s	cm
	Active material volume fraction	ε_s	-
	Porosity	ε_e	-
	Polymer phase volume fraction	ε_p	-
	Conductive filler volume fraction	ε_f	-
	Maximum solid phase concentration	$c_{s,max}$	$mol \cdot cm^{-3}$
Experimental measurement or estimation	Diffusion coefficient in solid	$D_{s,n}, D_{s,p}$	$cm^2 \cdot s^{-1}$
	Diffusion coefficient in electrolyte	D_e	$cm^2 \cdot s^{-1}$
	Stoichiometry at 0% SOC	x_0, y_0	-
	Stoichiometry at 100% SOC	x_{100}, y_{100}	-
	Film resistance	R_{film}	Ω
Literature	Exchange current density	i_0	$A \cdot cm^{-2}$
	Charge transfer coefficients	α_a, α_c	-
	Bruggeman exponent	P	-
	Electrolyte phase ionic conductivity	K	$S \cdot cm^{-1}$
	Li+ transference number	t_+^0	-
	Equilibrium potential of positive electrode	$U_{equ,p}$	-
	Equilibrium potential of negative electrode	$U_{equ,n}$	-

charging and discharging characteristics, and SOC. The objective functions are defined as the L^2 norm of the voltage errors for each SOC window and are minimized by the GA that results in a set of optimal parameters. Constant current charge and discharge profiles at different C-rates are used for the optimization process. The ROM with the automatically estimated parameters is validated against data obtained from two cycling tests. Additionally, the voltage errors are evaluated to assess the performance of the proposing procedure.

II. SENSITIVITY ANALYSIS

Out of 20 parameters, we selected eight parameters because of their dependency on operating conditions. They are the diffusion coefficients in solid and electrolyte phase ($D_{s,n}, D_{s,p}, D_e$), the stoichiometry numbers at 0% and 100% SOC of positive and negative equilibrium potentials ($x_0, y_0, x_{100}, y_{100}$), and a film resistance (R_{film}). Values of diffusion coefficients in the solid phase are dependent on the size and porosity of particles and temperature, while the value of the electrolyte is affected by temperature only. Besides, the values vary widely depending on different chemistries used for electrodes and electrolytes[9]. The stoichiometry numbers at 0% and 100% SOC are estimated so that the difference of the equilibrium potentials coincides with the measured OCV. The film resistance is a sum of the internal resistance of the cell, which is directly related to the battery terminal voltage.

The sensitivity analysis procedure is depicted in Fig. 1, which is performed automatically without being interrupted by any manual tuning. It includes two sub-procedures, deviation, and Jacobian analysis. The former is used to decide estimation sensitivity of parameters and the latter is to study the sensitivity of parameters in the SOC domain.

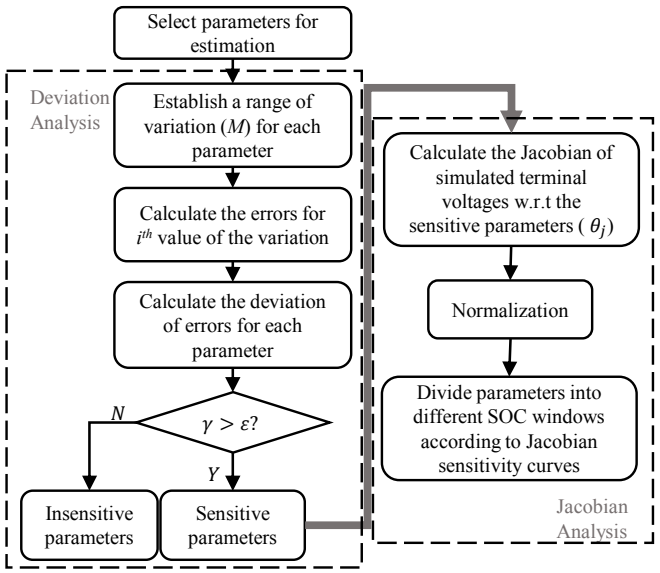

Fig. 1. Procedure of parameter sensitivity analysis

In order to decide the sensitivity of parameters, a range of variations of each parameter ($\boldsymbol{\theta}$) is arbitrarily set, and then several values within the range are selected and used to calculate terminal voltages of charge and discharge processes. The resulting relative error that is defined as a root-mean-square error is calculated for each simulation:

$$Error_i = \left(\frac{1}{N} \sum_{k=1}^{N} \left(\frac{V_{\exp}[k] - V_{sim,i}[k]}{V_{\exp}[k]} \right)^2 \right)^{\frac{1}{2}}, \quad (1)$$

where k and N denote the *kth* data point and the total number of data points, respectively. i represents the *ith* parameter variation. The subscripts *exp* and *sim* denote the voltage data obtained from experiments and simulations, respectively.

Then, a normalized deviation of the errors (γ) for each parameter is calculated as follows:

$$\gamma = \frac{\sum_{i=1}^{M} (Error_i - Error^*)}{M}, \quad (2)$$

where M is the total number of variations of parameters within its range. $Error^*$ is the error calculated from the reference value.

Finally, a threshold value (ε) is introduced to group insensitive and sensitive parameters, where ε is set as 10^{-4} with the standard deviation of 1% of the relative error.

The grouping results are listed in Table III, where the three sensitive parameters are the film resistance (R_{film}) and the solid phase diffusion coefficient of the positive and negative electrodes ($D_{s,p}$ and $D_{s,n}$).

On the other hand, a Jacobian analysis is carried out to determine the sensitivity characteristics of SOC domain. The Jacobian matrix, J, is calculated as the first order partial

TABLE III. NORMALIZED DEVIATION OF PARAMETERS

Symbol of parameters	Normalized deviation (γ)		Group
	Charge	*Discharge*	
$D_{s,p}$	0.0110	0.0011	Sensitive
$D_{s,n}$	1.196*e*−4	0.0047	Sensitive
D_e	8.212*e*−6	8.266*e*−7	Insensitive
x_0	4.275e-7	2.357e-6	Insensitive
y_0	2.454e-8	6.067e-8	Insensitive
x_{100}	1.122e-6	7.360e-7	Insensitive
y_{100}	1.803e-8	5.617e-7	Insensitive
R_{film}	0.0139	0.0529	Sensitive

derivative of the simulated terminal voltages for the sensitive parameters (θ_j), as follows:

$$J(\theta_j) = \frac{\partial V_{sim}}{\partial \theta_j}. \quad (3)$$

Due to the coupled equations showed in Table I, J cannot be expressed as an explicit form, so J is expressed using a difference method:

$$\frac{\partial V_{sim}}{\partial \theta_j} = \frac{V_{sim}\left(\theta_j + \Delta\theta_j\right) - V_{sim}\left(\theta_j\right)}{\Delta\theta_j}. \quad (4)$$

Because the Jacobian matrices have different orders of magnitudes for different parameters, a dimensionless expression is introduced:

$$J_{\theta_j} = \theta_j^* J\left(\theta_j\right), \quad (5)$$

where θ_j^* is the reference value of the corresponding parameter.

The dimensionless Jacobian matrices as a function of SOCs of the three sensitive parameters for 1C are plotted in Fig. 2 because of similar trends at other C-rates. For each of the parameters, the dimensionless Jacobian values vary with different SOCs. The higher the values are, the higher the sensitivity becomes. The magnitudes of $D_{s,p}$ are always greater than those of the $D_{s,n}$, which implies that the diffusion coefficient of the positive electrode is much more sensitive than that of the negative electrode. This is because the magnitudes of the equilibrium potential of the positive electrode are much greater than those of the negative electrode. The dimensionless Jacobian values of R_{film} is constant except for constant-voltage (CV) charge processes, which indicates that this parameter has the same sensitivity over the entire constant-current (CC) region. In addition, the signs of the Jacobian matrices at charge and discharge are always opposite. In other words, when altering the value of a parameter, if the charge curve goes upward, then the discharge curve goes downward, and vice versa. Therefore, both characteristics should be considered to find optimal values of parameters.

Based on the sensitivity characteristics in Fig. 2, the SOC domain is divided into two regions at discharge and three regions at charge depending upon the magnitudes of J_θ, as

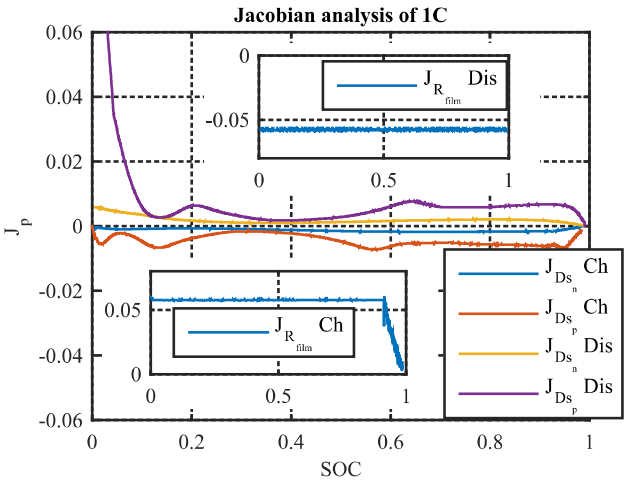

Fig. 2. Sensitivity characteristics of charge and discharge curve at 1C

TABLE IV. BEST SOC DOMAIN FOR ESTIMATION THE PARAMETERS

Region	I	II	III
SOC window	0-10%	10%-100%	CV (if applicable)
Charge	$D_{s,p}$, R_{film}	$D_{s,p}$, $D_{s,n}$, R_{film}	R_{film}
Discharge	$D_{s,p}$, R_{film}	$D_{s,p}$, $D_{s,n}$, R_{film}	_

shown in Table IV. For the charging process, region I starts from 0% SOC to 10%, where $D_{s,p}$ and R_{film} are considered, while in the region II, all three parameters are considered. Region III is in the CV mode, where R_{film} is considered since its sensitivity is not affected by the SOC. Similarly, the discharge process is divided in the same fashion as the charging process without the CV region.

III. OBJECTIVE FUNCTIONS

The objective functions are defined as the L^2 norm of the error given by the difference between the experimental and the simulation data for each SOC window. The SOC can be estimated using coulomb counting method, where an initial SOC and the input current are known for a charge or discharge profile.

$$\min_{\theta_j} \begin{cases} \sum_{k \in regionI} \left(V_{\exp}[k] - V_{sim,j}[k]\right)^2 \\ \sum_{k \in regionII} \left(V_{\exp}[k] - V_{sim,j}[k]\right)^2 \\ \sum_{k \in regionIII} \left(V_{\exp}[k] - V_{sim,j}[k]\right)^2 \end{cases} \quad (6)$$

$$\text{subject to } \theta_{j,\min} \le \theta_j \le \theta_{j,\max},$$

where V represents voltage that is the output of the model or of the experiment. $\theta_{i,min}$ and $\theta_{i,max}$ are lower and upper bounds of each parameter.

IV. OPTIMIZATION

A goal of optimization processes is to minimize the objective function. An overall estimation process with current as an input is depicted in Fig. 3. The voltage errors between experiment and simulation by ROM at every time step, and the corresponding SOCs, are calculated to obtain the value of the objective functions. Then the parameters of ROM are updated, and the estimation process is repeated until the stopping criterion is met. After the process has been completed, the model parameters are produced as outputs.

A number of optimization methods have been applied to solve the problem. These methods can be categorized into deterministic and stochastic approaches. The deterministic approach requires an explicit form of the first or second order derivatives. Due to its high sensitivity to the initial guess, it likely results in a local minimum. Conversely, a stochastic approach such as the GA guarantees a global optimization and its convergence speed can be increased using a multi-objective function. Thus, the GA was chosen.

To start, initial values of parameters are randomly selected within a given range determined empirically. Then the iteration process begins, in which a new generation of parameters produced replace the old generation based on the objective function. The new generation is produced in three ways: selection, crossover, and mutation. The selection is established based on the probability that is determined by the value of the objective function calculated at each iteration. The crossover and mutation reproduce new parameters by combining the old parameters with those randomly selected. Once the value of the objective function reaches one of two tolerances, either the minimum relative change in the objective function value or the number of generations that exceeds the maximum generation, this process is completed and exports the estimated parameters. The tolerances are set to 1e-4 and 50, respectively.

V. RESULTS AND ANALYSIS

The automatically estimated parameters are exported after applying the GA procedure. Units, starting ranges as well as estimated values are listed in Table V.

Even though the optimization takes place in the SOC domain, performance is examined in the time domain to check its practicability. Comparisons between simulations and experiments carried out with different C-rates show a good agreement, as plotted in Fig. 4.

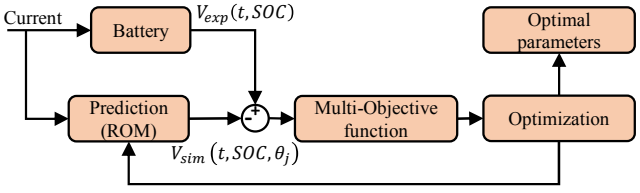

Fig. 3. Concept of parameter estimation process

TABLE V. ESTIMATED PARAMETERS

Symbol	Unit	Range		Estimated value
		min	*max*	
$D_{s,p}$	cm2·s-1	1e-11	1e-9	7.69e-10
$D_{s,n}$	cm2·s-1	1e-11	1e-9	9.50e-10
R_{film}	Ω	0	50	9.68

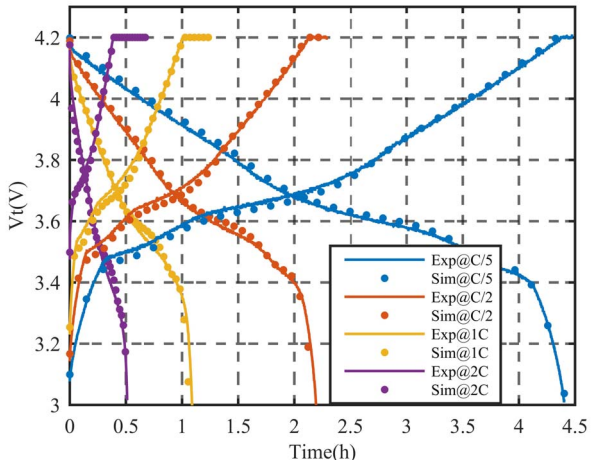

Fig. 4. Voltage comparisons between experiment and simulation of charge and discharge characteristics

In addition, two multiple-cycle tests have been conducted. The first test consists of 40 cycles of 2C CC charge and discharge. Fig. 5 shows comparisons of terminal voltages over time at every ten cycles, which shows very good agreement. The second test uses a current profile obtained from an electric vehicle driving cycle as shown in Fig. 6. A comparison of corresponding terminal voltages and its absolute error are plotted in Fig. 7, where the error remains within 12mV.

VI. Conclusion

In this paper, we have presented an automatic PE procedure that estimates parameters of ROM for BOL of LIBs. The procedure consists of grouping, sensitivity analyses and optimization of the parameters. We estimate three sensitive parameters from the ROM including the solid phase diffusion coefficients of the positive and negative electrodes, and the film resistance. The parameters are estimated from charge and discharge experimental data at C/5, C/2, 1C, and 2C. Then, a genetic algorithm is employed as an optimization method that considers a multi-objective function. Finally, the ROM with the optimized parameters is validated against experimental data obtained from a multiple-cycle and a driving cycle test. The results show a great agreement with the experimental data up to forty cycles. The overall voltage errors remain within 12mV.

The accomplishment of this paper can be summarized as follows:

- Sensitivity analysis is needed to reduce the estimation workload.
- Paring the GA with multi-objective functions improves the estimation efficiency.

Future work will focus on the transition from automatic PE to on-line PE. In addition, incorporating the aging model could be another critical task in the future studies.

Acknowledgment

The financial support from Hyundai NGV Company (HMC) is gratefully acknowledged.

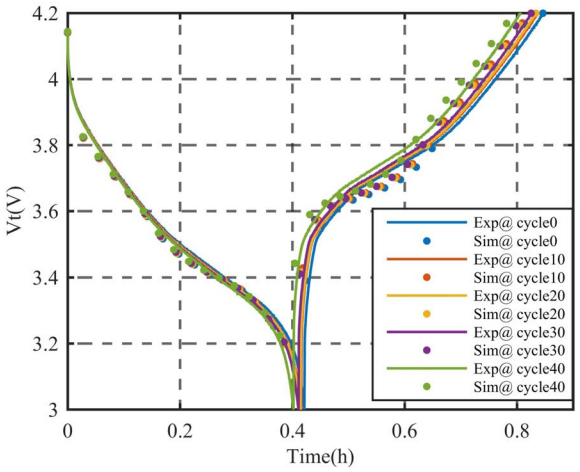

Fig. 5. Comparisons of terminal voltages for every ten cycles

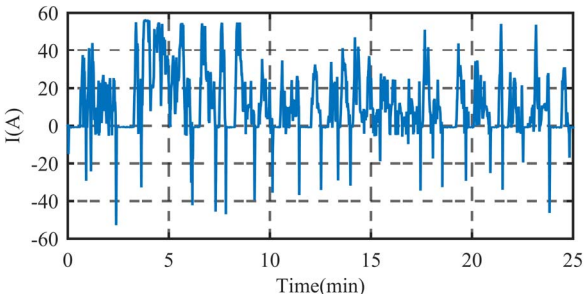

Fig. 6. Current profile of a driving cycle

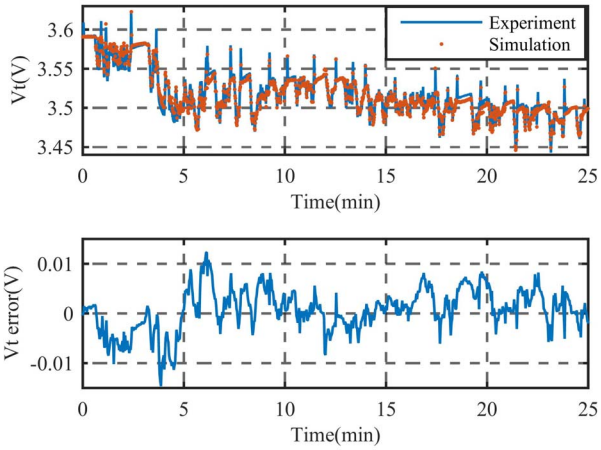

Fig. 7. A comparison of terminal voltages (upper) and its absolute errors (lower) of a driving cycle

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