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Rapid Prediction of the Open-Circuit-Voltage of Lithium Ion Batteries Based on an Effective Voltage Relaxation Model

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Received: 6 November 2018; Accepted: 4 December 2018; Published: 9 December 2018



Abstract: The open circuit voltage of lithium ion batteries in equilibrium state, as a vital thermodynamic characteristic parameter, is extensively studied for battery state estimation and management. However, the time-consuming relaxation process, usually for several hours or more, seriously hinders the widespread application of open circuit voltage. In this paper, a novel voltage relaxation model is proposed to predict the final open circuit voltage when the lithium ion batteries are in equilibrium state with a small amount of sample data in the first few minutes, based on the concentration polarization theory. The Nernst equation is introduced to describe the evolution of relaxation voltage. The accuracy and effectiveness of the model are verified using experimental data on lithium ion batteries with different kinds of electrodes (LiCoO₂/mesocarbon-microbead and LiFePO₄/graphite) under different working conditions. The validation results show that the presented model can fit the experimental results very well and the predicted values are quite accurate by taking only 5 min or less. The satisfying results suggest that the introduction of concentration polarization theory might provide researchers an alternative model form to establish voltage relaxation models.

Keywords: lithium ion batteries; open circuit voltage; concentration polarization theory; universal relaxation model; rapid prediction

1. Introduction

Due to their unique advantages in energy/power density and cycle life, rechargeable lithium-ion batteries (LIBs) are preferred in energy storage devices for most applications in portable electronics, electric vehicles (EV) and grid energy storage [1–3]. In order to ensure the reliable and safe operation of LIBs, accurate online estimation of battery states, including state of charge (SOC) [4–6], state of health (SOH) [7–9] and state of energy (SOE) [10–12], is the most crucial task for a battery management system (BMS).

As a vital thermodynamic characteristic parameter reflecting the internal state of LIBs, open circuit voltage (OCV) of LIBs in equilibrium state (*e*-OCV) plays an important role in battery state estimation and BMS since *e*-OCV depends on the essential properties of electrode material and electrolyte as well as the concentration of lithium intercalated in active electrode material [13–15]. Thus, *e*-OCV can



be employed to estimate the SOC of LIBs because the relationship between *e*-OCV and SOC is very apparent and nearly monotonous for most of LIBs [16,17]. For example, the *e*-OCV -SOC curve or the 3-dimonsional *e*- OCV-SOC-T surface are obtained in the lab beforehand as a look-up table for SOC estimation [18]. The *e*-OCV can be predicted using models or other techniques and then the SOC can be estimated based on the look-up table [19]. This method is the most commonly used correction method for accurate SOC estimation. *e*-OCV can also be used to estimate the SOH of LIBs because the aging of LIBs is often associated with loss of lithium inventory, degradation of active material and increase of resistance, which would inevitably affect *e*-OCV value [20]. Therefore, accurate and rapid estimation of *e*-OCV is of importance for optimum operation of LIBs.

However, it may take a quite long time (generally > 3 h) for LIBs to reach a complete equilibrium state after the current interruption, as shown in Figure 1, especially when they are operated at high charge/discharge rates and in low temperature with large SOC shifts [21,22]. This shortcoming has seriously limited the application of e-OCV. To address this problem, a few approaches including semi-empirical models, pure empirical models and equivalent circuit models were presented to predict e-OCV within a relatively short time. For example, Bergveld et al. [23] proposed a pure empirical voltage relaxation fitting-model for LIBs. Unfortunately, this model can only fit a certain type of LIBs, and its accuracy is far from satisfying when being applied to other LIBs. Unterrieder et al. [24] developed a mathematical model based on nonlinear least square estimation to describe the OCV transients. The fitted results of the model for the primary phase of the voltage relaxation curves are far from satisfying. More recently, equivalent circuit models have attracted much attention for e-OCV estimation. Waag et al. [25] presented a voltage relaxation fitting method based on a fifth-order equivalent circuit model to estimate e-OCV by taking the theoretical diffusion process into consideration, and successfully applied it to fast estimation of e-OCV. Nevertheless, it is much more sophisticated and did not always fit the measured data well. Pei [13] developed a voltage relaxation model based on a parameters-varying second-order resistance-capacitance model. It takes 20 min at least to predict *e*-OCV, which is time consuming for real application.



Figure 1. A schematic diagram of the voltage relaxation process of a LiCoO₂/graphite battery after current interruption.

The basic idea of the above studies is to build relaxation process models, whose parameters are determined by a presupposed algorithm using the data measured in the first few minutes. Then, *e*-OCV can be obtained by extrapolation. However, most of these models cannot describe the transients of the OCV relaxation behavior very well and they are either non-universal or still time-consuming which further makes the application confining. Therefore, developing a more effective and accurate *e*-OCV estimation model is still urgent and challenging.

This work aims at developing a semi-empirical and general model that can be put into practical application to predict the *e*-OCV value within a much shorter time. Previous studies [21,22] show that

the time-consuming voltage relaxation process is mainly governed by temperature, charge/discharge rate, aging degree and ultimately the diffusion of lithium ion. Thus, we adopt a physics-based electrochemical model to illustrate LIBs, as shown in Figure 2 [26]. Then we deduce the OCV relaxation model by incorporating the diffusion theory and electrochemical reaction kinetics. The introduction of physicochemical principle provides us an approximate and general format of the mathematical model that ensures the generality and estimation accuracy of the OCV prediction model. In Section 4, the generality and accuracy of this model are verified on LIBs for different active materials, temperatures, depth of discharge (DOD) and charge/discharge rates.



Figure 2. Schematic illustration of a lithium ion battery model.

The work is organized as follows: Section 1 presents a brief review of the researches which are intended to develop effective approaches to obtain the *e*-OCV rapidly and analyzes the urgency of establishing an alternative voltage prediction model. Section 2 describes in details the mathematical model of the voltage relaxation. The experimental setup is specified in Section 3 and the validation results and discuss are shown in Section 4. The conclusions are given in Section 5.

2. Mathematical Model of OCV Relaxation Process

2.1. Model Description

It is generally known that the electric field and concentration differences promote the diffusion of lithium ion in LIBs. This paper concentrates on the voltage relaxation process after the charging/discharging of LIBs is interrupted, which means that only the concentration difference of lithium ion is taken into consideration.

For our modelling, we just focus on the simulation of the voltage relaxation behavior after a few seconds of the current interruption. The voltage transients during this period are mainly dominated by concentration polarization voltage since the time constants of the ohmic voltage drop and electrochemical polarization is so small that they can be out of consideration in the following relaxation process. So we firstly divide the diffusion path of lithium ion into infinite elements. Obviously, the concentration of lithium ion between each segment and adjacent one are different, as shown in Figure 2. Based on the concentration potential theory [27], we could adopt the Nernst equation to calculate the concentration polarization voltage between two adjacent segments.

$$\Delta V_i = \frac{RT}{nF} \ln \frac{c_i}{c_{i+1}}, i = 1, 2 \cdots, m \tag{1}$$

where *R* is the universal gas constant, *T* is temperature, *n* is the number of electrons involved in the virtual electrode reaction and as for lithium ion, we take n = 1. *F* is Faraday's constant and c_i is the concentration of diffusible lithium ion in corresponding segments. According to the Fick's second law, c_i is a function of time *t* and distance *x* from the electrode. We here transform Equation (1) to another form with time *t* as the only independent variable since the concentration of the diffusible lithium ion is time-dependent before LIBs reach equilibrium state, as shown by Equation (2):

$$\Delta V_i(t) = \frac{RT}{F} \ln \frac{c_i(t)}{c_{i+1}(t)}, i = 1, 2 \cdots, m$$
(2)

The segmentation treatment makes it rational that treating the LIB as battery unit which is series connected. Therefore, the total concentration polarization voltage of the LIBs can be expressed as Equation (3):

$$\Delta V(t) = \Delta V_1(t) + \Delta V_2(t) + \dots + \Delta V_{m-1}(t) + \Delta V_m(t)$$
(3)

Substituting Equation (2) into Equation (3):

$$\Delta V(t) = \frac{RT}{F} \ln \frac{c_1(t)}{c_2(t)} + \frac{RT}{F} \ln \frac{c_2(t)}{c_3(t)} + \dots + \frac{RT}{F} \ln \frac{c_{m-2}(t)}{c_{m-1}(t)} + \frac{RT}{F} \ln \frac{c_{m-1}(t)}{c_m(t)}$$

$$= \frac{RT}{F} \ln \left(\frac{c_1(t)}{c_2(t)} \cdot \frac{c_2(t)}{c_3(t)} \cdot \dots \cdot \frac{c_{m-2}(t)}{c_{m-1}(t)} \cdot \frac{c_{m-1}(t)}{c_m(t)} \right)$$

$$= \frac{RT}{F} \ln \left(\frac{c_1(t)}{c_m(t)} \right)$$
(4)

It should be noted that $\Delta V(t)$ is positive when LIBs are at discharged state (negative for charged state) before the current is interrupted.

What's more, the voltage when LIBs are in equilibrium state is defined as the *e*-OCV, indicated as V_o , so we get the OCV expression of LIBs:

$$U(t) = V_0 - \Delta V(t) \tag{5}$$

Substituting Equation (4) into Equation (5):

$$U(t) = V_o - \frac{RT}{F} \ln\left(\frac{c_1(t)}{c_m(t)}\right)$$
(6)

The general formula is rewritten as:

$$U(t) = V_o - \frac{RT}{F} \ln[f(t)]$$
(7)

where f(t) is a function of t.

The concentration theory and Equations (1)–(7) provide us a general model format, from the perspective of electrochemical theory, to express the relaxation process of OCV. And as we can see that in Ref. [28], the concentration of ion on the surface of the electrodes can be expressed as power function of time. Therefore, we can take Equation (8) to represent the expression of f(t) in Equation (7):

$$f(t) = \kappa \cdot t^{\gamma} \tag{8}$$

where κ and γ are two parameters which are associated with the property of the electrodes and electrolyte, respectively, and they are all temperature-dependent [28]. However, it should be noted

that the function of the ion concentration is deduced based some ideal assumptions and it's infeasible and impractical here to still deduce the specific expression of f(t) in Equation (7) exactly based on the physical and chemical mechanism, since we aim to develop a simple and applicable voltage relaxation model to predict the OCV within a short period of time. For the actual situation studied in this work, considering those factors mentioned above, we can say that these two parameters are time-dependent since the property of the electrode surface and electrolyte vary with time, so we utilize $\kappa(t)$ and $\gamma(t)$ to substitute the two parameters and get:

$$f(t) = \kappa(t) \cdot t^{\gamma(t)} \tag{9}$$

Substituting Equation (9) into Equation (7), we get:

$$U(t) = V_0 - \frac{RT}{F} \ln \left[\kappa(t) \cdot t^{\gamma(t)} \right]$$

= $V_0 - \frac{RT}{F} \gamma(t) \ln(t) - \frac{RT}{F} \ln[\kappa(t)]$ (10)

Given the fact that the properties of the electrodes change only a little between the points when the current is interrupted and the cells reach equilibrium state, so we just take the third term in Equation (10) as an adjustment factor which is represented by a power function to improve the prediction accuracy of the model. The property of the electrolyte near the electrodes during this period changes a lot and, similar to the expression form of the ion concentration, we adopt power function to characterize its changing property with time. And on the basis of these analyses, we obtain the final expression of the voltage relaxation model as Equation (11):

$$U(t) = V_0 - k_3 \cdot t^{k_4} \ln(t) - k_1 \cdot t^{k_2}$$
(11)

where $k_1 \cdot t^{k_2} = \frac{RT}{F} \ln[\kappa(t)]$, $k_3 \cdot t^{k_4} = \frac{RT}{F} \gamma(t)$ and $k_j(j = 1, 2, 3, 4)$ are the model parameters to be fitted.

2.2. Parameters Identification Method

The proper set of V_o and $k_j(j = 1, 2, 3, 4)$ need to be identified using the data recorded in the voltage relaxation process. To implement the identification algorithm, we first restrict the value of V_o to a certain scope to improve the reliability of model because it represents *e*-OCV of the LIB tested. This scope should depend on the specific battery system and state. The parameters are then obtained by fitting the model to the measured data by the least square method [29]. The judgement function for optimization is the root mean square error (*RMSE*) between the fitted voltage in the model and the measured voltage in the experiment as defined by Equation (12):

$$RMSE = \sqrt{\frac{1}{N} \sum_{n=1}^{N} \left(U_{fitted}(t_n) - U_{measured}(t_n) \right)^2}$$
(12)

where *N* is sample size, and n is a sample point.

3. Experimental Setup

In this paper, validation tests are conducted on two different kinds of LIBs and three factors including SOC, charge/discharge rate and temperature are taken into consideration. Two of the used cells are the prismatic 1.15 Ah LIB (Cell-1 and Cell-3) with LiCoO₂ as cathode and mesocarbon microbead (MCMB) as anode, and the other one is the prismatic 0.67 Ah LIB (cell-2) with LiFePO₄ as cathode and graphite as anode. The electrolyte in both kinds of LIBs is comprised of 1 mol L-1 LiPF6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume ratio). The full charge/discharge (100% DOD) corresponds to voltage from 3.0 V to 4.2 V for LiCoO₂/MCMB battery and 2.5 V to 3.7 V for LiFePO₄/graphite battery. The specific details of these two cells are presented in Table 1.

Parameter	Cell 1,3	Cell 2
Geometry	Prismatic	Prismatic
Active material	LiCoO ₂ /MCMB	LiFePO ₄ /graphite
Nominal capacity (Ah)	1.15	0.67
Nominal voltage (V)	3.7	3.2
Operating voltage range (V)	3–4.2	2.5–3.7
Characterization rate (C)	0.2	1/3

Table 1. Specifications of the three used cells.

Prior to the validation experiments, capacity characterization tests including three constant current-constant voltage charge and constant current discharge cycles were carried out on the three cells. The procedures of the characterization test are as follows: for the $LiCoO_2/MCMB$ cells under test, firstly they were fully charged with 0.2 C rate until the voltage reached 4.2 V and held at 4.2 V until the charge rate decreased below 0.02 C. Then they were discharged with 0.2 C rate until the cell voltage decreased to 3.0 V. For LiFePO₄/graphite cells, every charge/discharge cycle includes a full charge with C/3 rate until battery voltage increased to 3.7 V and holding at 3.7 V until the charge rate reduces below 0.02 C, and a full discharge with C/3 until the battery voltage drops to 2.5 V.

After the initial characterization tests, Cell-1 and Cell-2 were fully charged with constant current-constant voltage mode mentioned above. The constant charge rates were both 0.5 C, and the cut-off current rates were both 0.05 C during the constant voltage charge phase for these two cells. It is worth noting that the full charge mode for Cell-1 and Cell-2 during all the following tests is the same and in order to reduce duplication, so we will not describe the full charge step again. Then Cell-1 was discharged to 90%, 70%, 50% and 30% SOC sequentially with 0.25 C followed by a 3 h rest at every corresponding SOC point. Considering the influencing factors of discharge current rates, the fully charged Cell-1 was discharged to 70% SOC followed by a 3 h rest with different current rates including 0.5 C, 1.0 C and 1.5 C. All the experiments described above were performed at 35 °C. As supplementary, additional validation tests when the cell was in charged state (charged with different current rates) were also carried out on a LCO/MCMB cell (Cell-3) and the temperature was controlled to 25 °C. Specifically, the cells were discharged to the lower cut-off voltage of 3.0 V with constant current rates (including 0.25 C, 0.5 C, 1.0 C and 1.5 C) followed by a 3 h relaxation process. Prior to the next charge test with a different current rate, it was discharged again to 3.0 V.

Then, the voltage relaxation behavior of Cell-1 at different temperature was studied and the setup is detailed as follows: the fully charged Cell-1 at 35 °C was conditioned at 25 °C and 40 °C for 3 h and then discharged to 70% SOC with 0.5 C followed by a 3 h rest, respectively. In order to verify the effectiveness of our model at low temperature, we studied the voltage relaxation process of cells discharged at different temperatures (including 15 °C, 5 °C, -5 °C and -15 °C). Particularly, Cell-3 were fully-charged every time with CC-CV regime (0.5 C to 4.2 V, 4.2 V to 0.02 C) at 25 °C and discharged to 70% SOC with 0.5 C at the temperatures mentioned above. It should be noted that prior to the charge or discharge process, the cells were relaxed at the corresponding temperature for at least 3 h. Furthermore, the voltage relaxation data of LiFePO₄/graphite battery (Cell-2) at 35 °C was extracted at 80% SOC with 0.5 C discharge rate. It should be noted that the data sampling rate during the test was set 1 s or voltage increment ≥ 5 mV.

All electrochemical tests were carried out using a NEWARE Battery Testing System (5 V, 6 A, NEWARE Electronics Co., Ltd., Shenzhen, China) with a voltage measurement accuracy of $\pm 0.1\%$ and the sampling rate was 1 s. A BILON DNP–9052 temperature-controlled cabinet ((RT + 5) ~65 °C, BILON Laboratory Equipment Co., Ltd., Beijing, China) with a measurement accuracy of ± 0.5 °C was used to control the temperature of the test for Cell-1. The temperature for the tests of Cell-3 was controlled by a temperature chamber (-70~+150 °C) manufactured by Chongqing Yinhe Experimental Equipment Co. Ltd. (Chongqing, China). The test platform can be seen in Figure 3.



Figure 3. Schematic diagram of the experimental platform.

4. Results and Discussion

For validation, we applied the data collected within 5 min to our model to predict e-OCV and we just showed a portion of validated results. Figure 4a,b present the validation results of LiCoO₂/MCMB battery (Cell-1) at 70% SOC and LiFePO₄/graphite battery at 80% SOC. The blue and the red solid lines are the measured and the fitted relaxation voltage results, while the blue and the red dot lines are the measured and the predicted e-OCV, respectively. The two LIBs (Cell-1 and Cell-2) were discharged at 0.5 C rate and temperature was 35 °C. It can be seen clearly that the model fits the measured curves very well and the measured data and predicted value are very close. Specifically, the measured and predicted e-OCV is 3.8833 V and 3.8831 V for LCO/MCMB battery (Cell-1), and 3.3274 V and 3.3271 V for LFP/graphite battery. The corresponding absolute errors are 0.2 mV and 0.3 mV, as shown in Table 2, which are negligible since the fourth figure is just an estimated value. In addition, the supplementary validation result for anther aged cell, which is consisted of NCA and graphite, is presented in Figure S4 in the Supplementary Materials. The SOC of the cell is 73% and the SOH is 79%. For simplicity, the details about the supplementary experiments can be found in the Supplementary Materials. Satisfyingly, the predicted result agrees well with the measured data with an absolute error of 0.7 mV. Therefore, we can deduce preliminarily that our presented model is effective for other battery systems with different active materials at different SOH.

Table 2. Details of the validation results for LCO/MCMB (Cell-1) and LFP/Graphite batt	ery
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Active Material	Measured (V)	Predicted (V)	Absolute Error (V)	Relative Error (%)
LCO/MCMB	3.8833	3.8831	0.0002	0.005
LFP/Graphite	3.3274	3.3271	0.0003	0.009

Figure 5 shows the measured and fitted voltage relaxation curves of LCO/MCMB battery (Cell-1) at four different SOC points. The discharge rate was 0.25 C and temperature was 35 °C. The measured data is marked in blue while the fitted results are marked in red. We can find that the model fits the measured data with very high accuracy although the experimental data fluctuates a little. As can be seen in Table 3, the measured *e*-OCV values are 4.0085 V, 3.8826 V, 3.8061 V, and 3.7475 V, while the predicted ones are 4.0083 V, 3.8824 V, 3.8076 V, and 3.7477 V, respectively. The measured results and the predicted ones are almost equal to each other for most situations when the battery was in 90%, 70% and 30% SOC. The maximum error 1.5 mV is reached when the cell was in 50% SOC. The larger error is probably caused by the larger fluctuations. Nonetheless, we can still say that it is small enough for

the application. We believe that the validated results suggest that our model is applicable for cells in a good SOH within the whole SOC range.



(a) Cell-1-LCO/MCMB 70% SOC 35 °C

Figure 4. The measured and predicted voltage relaxation results of: (**a**) LCO/MCMB battery (Cell-1) at 70% SOC, and (**b**) LFP/Graphite battery at 80% SOC. They were discharged with 0.5 C at 35 °C before the current interruption.

SOC (%)	Measured (V)	Predicted (V)	Absolute Error (V)	Relative Error (%)
90	4.0085	4.0083	0.0002	0.005
70	3.8826	3.8824	0.0002	0.005
50	3.8061	3.8076	0.0015	0.039
30	3.7475	3.7477	0.0002	0.005

Table 3. Specifications of the validation results of LCO/MCMB battery (Cell-1) at different SOCs.

Figure 6a,b illustrate the verification results of LCO/MCMB battery (Cell-1) at 40 °C and 25 °C, Figure 6c–f are the validation results of LCO/MCMB battery (Cell-3) at 15 °C, 5 °C, -5 °C and -15 °C, respectively. The blue lines represent the measured results and the red ones are the fitted results. The SOC is 70% and the discharge rate was 0.5 C. Obviously, the fitted results of the model fits to the voltage curves are satisfying and, as shown in Table 4, the measured *e*-OCV are 3.8833 V, 3.8780 V, 3.9360 V, 3.9304 V, 3.9183 V and 3.9035 V while the predicted results are 3.8838 V, 3.8779 V, 3.9318 V, 3.9330 V, 3.9200 V and 3.9060 V at 40 °C, 25 °C, 15 °C, 5 °C, -5 °C and -15 °C, respectively. The predicted and measured results are approximate to each other with a maximum error of 4.2 mV and an average error of 1.9 mV which are within the scope of measurement accuracy (5 mV). In combination with the result at 35 °C shown in Figure 4a, we can conclude that the model is applicable for various temperature conditions. We can find that the *e*-OCV of Cell 3 are greater than that of Cell-1 with

35

25

15

5

-5

-15

3.8826

3.8780

3.9360

3.9304

3.9183

3.9035

the same SOC of 70%, even at lower temperature. It should be noted here, on one hand, the charge regimes for Cell-1 and Cell-3 are different. The cut-off current rate during the CV process was 0.05 C for Cell-1 while the value for Cell-3 was 0.02 C, which means that more capacity was charged into Cell-3 during the charging process. On the other hand, Cell-3 is fresh while Cell-1 had been stored for about two years before the experiments were conducted on it. These two points might be the reason for this phenomenon.



Figure 5. The measured and fitted voltage relaxation results of LCO/MCMB battery (Cell-1) at different SOC points: (**a**) 90%, (**b**) 70%, (**c**) 50%, and (**d**) 30%. It was discharged with 0.25 C at 35 °C.

Temperature (°C)	Measured (V)	Predicted (V)	Absolute Error (V)	Relative Error (%)
40	3 8833	3 8838	0.0005	0.013

3.8824

3.8779

3.9318

3.9330

3.9200

3.9060

0.0002

0.0001

0.0042

0.0026

0.0017

0.0025

0.005

0.003

0.107

0.067

0.043

0.064

Table 4. Details of the verification results of LCO/MCMB battery at different temperatures.

Figure 7 shows the validation results of LCO/MCMB battery (Cell-1) at 70% SOC and 35 $^\circ$ C for
discharge rates of 1.0 C and 1.5 C. The experimental results are marked in blue and the predicted
results are marked in red. As listed in Table 5, the measured e-OCV values are 3.8833 V and 3.8833 V,
while the predicted results are 3.8828 V and 3.8837 V, respectively. The maximal absolute error is only
0.5 mV which is smaller than the measurement error of the test device. Combining with the results
shown in Figures 4a and 5b, we can deduce that the applicability of the OCV relaxation model is
completely unaffected by discharge rates for new cells.



Figure 6. Results of the measured and fitted relaxation voltage of LCO/MCMB battery with 70% SOC at different temperatures: (a) 40 °C, (b) 25 °C, (c) 15 °C, (d) 5 °C, (e) -5 °C, (f) -15 °C. The discharge rate was 0.5 C. (a,b) were extracted from Cell 1 and (c–f) were extracted from Cell 3 as supplementary experiments.



Figure 7. Validation results of LCO/MCMB battery discharged with different current rates: (**a**) 1.0 C and (**b**) 1.5 C. The SOC was 70% and the temperature was 35 °C.

Table 5. Details of the validation results of LCO/MCMB battery with different discharge rates.

Discharge Rate (C)	Measured (V)	Predicted (V)	Absolute Error (V)	Relative Error (%)
0.25	3.8833	3.8831	0.0002	0.005
0.5	3.8826	3.8824	0.0002	0.005
1.0	3.8833	3.8828	0.0005	0.013
1.5	3.8833	3.8837	0.0004	0.010

What's more, we analyzed the prediction performance of our model for the battery in charged state. Figure 8 is the validation results of LCO/MCMB battery (Cell-3) in charged state with 70% SOC and current rates of 0.25 C, 0.5 C, 1.0 C and 1.5 C were taken into consideration. The temperature was 25 °C. As shown in Figure 8, the modelled results shown in red are almost identical with the measured voltage curves signed in blue. The measured *e*-OCV when the current rates are 0.25 C, 0.5 C, 1.0 C and 1.5 C are 3.9506 V, 3.9555 V, 3.9583 V and 3.9596 V, respectively. And the corresponding predicted results are 3.9520 V, 3.9531 V, 3.9545 V and 3.9541 V, respectively. The mean error is 3.3 mV which is small enough for application, as listed in Table 6. The maximum absolute error for situation when the charge rate is 1.5 C is 0.0055 V which is also acceptable since the measurement accuracy of our equipment is 5 mV. We speculate that it is because of the higher heat generation at higher charge rate. Meanwhile, we would like to let you know that the maximum charge rate for our self-designed cells

are suggested to be 0.5 C. Therefore, we could come to a conclusion that our model is suitable for situation when the cells are charged with different current rates.



(a) R = 0.25C Cell-3-LCO/MCMB 70% SOC 25°C (b) R = 0.5C

Figure 8. The validation result when the LCO/MCMB battery (Cell-3) is in charged state.

Charge Rate (C)	Measured (V)	Predicted (V)	Absolute Error (V)	Relative Error (%)
0.25	3.9506	3.9520	0.0014	0.035
0.5	3.9555	3.9531	0.0024	0.061
1.0	3.9583	3.9545	0.0038	0.096
1.5	3.9596	3.9541	0.0055	0.139

Table 6. Validation results when the LCO/MCMB battery (Cell-3) is in charged state.

As shown in Figures 5 and 8, some of the measured data fluctuates greatly over time which means that the measurement might be influenced by some external factors. Correspondingly, the prediction errors are greater. However, as we can see from Tables 2–6, almost all the relative errors (except two situations) are smaller than the accuracy error of the measurement equipment (0.1%). The satisfying prediction accuracy though with relatively larger prediction errors suggests that the method has high fault tolerance to the equipment noise and other measurement errors. And the measurement errors would not propagate to the prediction errors since the input of this model is independent.

Additionally, the results of model parameters are shown in Supplementary Materials. Figures S1–S3 show the results of the model parameters for LCO/MCMB battery (Cell-1) at different SOC points, temperatures and discharge rates respectively. Interestingly, it can be found that parameter k_1 in Equation (11) is always positive while parameters k_2 , k_3 and k_4 are negative for all these situations.

The relationships between parameter k_j (j = 1, 2, 3, 4) and the influencing factors are, except for three non-normal points, approximately monotonic. Specifically, k_1 increases with increasing SOC and discharge rates and decreases with increasing temperature, and the results for k_2 is just the reverse. As the value of the influencing factors increase, k_4 decreases gradually and the degree of the variation is relatively small. The effect of temperature and discharge rate on parameter k_3 is bigger than that of SOC. k_3 increases with increasing temperature and decreases with increasing discharge rates obviously, and the correlation between and these two factors is linear, approximately, but k_3 increases only a little with increasing SOC. We infer that parameter k_3 , as the pre-factor of the logarithmic function, mainly reflects the voltage relaxation process of LIBs and SOC has few influences on the relaxation of voltage. The physically meaningful dependencies of the model parameters on the influencing factors demonstrate the physical rationality of our model.

5. Conclusions

In this paper, we have proposed a novel voltage relaxation model for rapid *e*-OCV prediction of LIBs at high values of the SOH. We divided the LIBs in the radial direction into infinite segments and designed virtual concentration cell between every two adjacent segments. Based on the diffusion theory and electrochemical reaction theory, the Nernst equation was employed to express the concentration polarization voltage. Furthermore, a power approximation [9,30,31] which is usually used for model development was utilized to establish the prediction model.

Then the effectiveness and accuracy of the presented model were validated by two kinds of LIBs under different working conditions. The satisfactory curve-fitting results, along with the strongly-related relationships between the model parameters and the influencing factors as shown in Figures S1–S3 in the Supplementary Materials, suggest that the treatment method for the LIBs and the deduction approach of the voltage relaxation model presented is rational. The satisfying fitting results also manifest that this approach probably provides us a rational expression format for further development of voltage relaxation model. The negligible prediction errors for all these situations demonstrate that our voltage relaxation model is effective and accurate enough for *e*-OCV prediction. What's more, our approach can greatly shorten the relaxation time (<5 min) needed in conventional methods (>20 min) [13]. And the calculation process is realized by the simple least square fitting which greatly reduces the complexity of calculation. Therefore, the model parameters can be easily identified online, which makes it applicable for Battery Management Systems (BMS). Also, the detailed validation of our method will be tested for LIBs under lower values of the SOH in a future study.

6. Patents

Patent [No: CN105467328A] resulting from the work reported in this manuscript was issued.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/11/12/3444/ s1, Figure S1: Results of the model parameters for LCO/MCMB battery at different SOC points, Figure S2: Results of the model parameters for LCO/MCMB battery at different temperatures, Figure S3: Results of the model parameters for LCO/MCMB battery at different discharge rates, Figure S4: Validation result for an aged NCA/Graphite battery with SOH being 79% at 73% SOC.

Author Contributions: J.Y. reviewed the literature, designed the experiments and performed part of the tests, and wrote the manuscript. T.W. performed the supplementary experiments. C.D., Y.G., X.C., P.Z., Y.M. and J.W. reviewed and revised the original draft. Supervision, G.Y.; project administration, J.X; funding acquisition, B.L.

Funding: This work is partially funded by the National Key R&D Program of China [No: 2018YFB0905301].

Acknowledgments: We would like to thank Shen Bin and Lv Taolin for providing useful suggestions to improve the quality of this paper.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

OCV	Open circuit voltage
BMS	Battery management system
CC-CV	Constant current-constant voltage
DEC	Diethyl carbonate
DOD	Depth of discharge
EC	Ethylene carbonate
e-OCV	Open circuit voltage in in equilibrium state
EV	Electric vehicles
LCO	LiCoO ₂
LFP	LiFePO ₄
LIBs	Lithium ion batteries
MCMB	Mesocarbon microbead
NCA	LiNi _x Co _y Al _z O ₂
P2D	Pseudo-two-dimensional
RMSE	Root mean square error
RT	Room temperature
SOC	State of charge
SOE	State of energy
SOH	State of health
U	Terminal voltage
F	Faraday's constant
Ν	Sample size
R	The universal gas constant
Т	Temperature
c _i	Concentration of lithium ion
i, j	Serial number
п	Number of electrons transferred
t	Time
ΔV	Voltage difference

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