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Development of a voltage relaxation model for rapid open-circuit voltage prediction in lithium-ion batteries

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HIGHLIGHTS

- Discover that diffusion time constant is a linear function of open-circuit time.
- Established a new voltage relaxation model with good curve-fitting performance.
- Presented a rapid, adaptive and online OCV prediction method.
- Shorten the waiting time from traditional 20 h to 20 min with the new method.

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ABSTRACT

The open-circuit voltage (OCV) of a battery, as a crucial characteristic parameter, is widely used in many aspects of battery technology, such as electrode material mechanism analysis, battery performance/state estimation and working process management. However, the applications of OCV are severely limited due to the need for a long rest time for full relaxation. In this paper, a rapid OCV prediction method is proposed to predict the final static OCV in a few minutes using linear regression techniques, based on a new mathematical model developed from an improvement on a second-order resistance–capacitance (RC) model. As the improvement, an important discovery is demonstrated by experimental investigation and data analysis: the relaxation time (i.e., time constant) of the diffusion circuit of the second-order RC model is not a fixed constant, unlike an intrinsic value for a given material, but an apparent linear function of the open-circuit time. This improvement enables the new model to track the actual relaxation process very well. The accuracy and the rapidity of the new model and proposed method are validated with working-condition experimental data on battery cells with different cathodes, and the results of OCV prediction are very accurate (errors below 1 mV in 20 min).

1. Introduction

Rechargeable batteries play a significant role in powering many portable applications that have high electric power requirements. For electric vehicles (EVs) (including battery electric vehicles, hybrid electric vehicles and plug-in hybrid electric vehicles) and mobile electronics (such as mobile phones and laptops), the use of a lithium-ion battery as a storage system is currently the best choice based on comprehensive consideration of its energy and power density and cycle-life [1].

The open-circuit voltage (OCV) of the lithium-ion battery, a crucial characteristic parameter, reflects the battery's inertial status and plays an important role in many aspects of battery technology, such as electrode material mechanism analysis, battery performance/state estimation and working process management [2–9]. Because lithium-ion battery OCV depends on the electrode material and the amount of lithium intercalation in it [2,3], the battery OCV can not only be used to analyze the relative electron energies of the electrode materials but can also be used to estimate the state-of-charge (SOC) of the batteries, which indicates the available capacity of the cells [4–6]. The OCV can also be used to estimate the batteries' state-of-health (SOH) because the battery OCV decay occurs only in the high-SOC range during the battery aging process [7]. Additionally, the OCV is used as an important judge basis for cell balancing strategy technology [8,9]. Thus, an accurate determination of the OCV is requested to enable management of the battery in its optimal state.

The battery voltage only equals the static OCV when the battery is under open-circuit conditions and the voltage has been relaxed to its equilibrium. During the rest period, the impacts of the

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measurement current and the side-reaction can be neglected, but a long rest time is always needed (e.g., 20 h). Unfortunately, the long waiting time severely limits the application of the OCV, especially for online working conditions. To overcome this shortcoming of the conventional rest method for the OCV, some studies have been performed to shorten the time for obtaining the OCV in equilibrium [5,6,8,10–12]. A few straightforward methods are presented for lead-acid batteries in earlier papers, e.g., the asymptotes method [10] and the *dV*/*dt* method [11]. However, as limited by the use of fixed parameters, these techniques are not appropriate for various working conditions such as different temperatures and SOCs. For lithium-ion cells, a few methods are proposed to predict the final OCV based on the battery voltage and the time measurements of the first several minutes of the relaxation process. In these methods, for simulating the voltage relaxation process, a few mathematical models are presented, including empirical models and equivalent circuit models. In Refs. [5,6], two empirical models are proposed by curve fitting. However, both of them lack a reasonable physical interpretation and the corresponding OCV prediction methods do not always have a reasonable computational effort for an online application. As for a more reasonable physical interpretation, a conventional second-order resistance–capacitance (RC) model with a fixed time constant is used in Ref. [8], but this model does not fit the measured relaxation curve well enough. Additionally, based on a modified second-order RC model, a rapid test-procedure method to derive the OCV is described in Ref. [12]. However, when the method is used in an online application, a few millivolts error of the OCV prediction probably occurs, because the diffusion overpotential of the proposed model is taken as a constant value.

This work aims at developing an accurate and reasonable voltage relaxation model and a low-complexity OCV prediction method. Depending on the study of the relaxation process of the diffusion overpotential, which is caused by the insufficient transport of the reactants and dominates during most of the time of the entire relaxation process, the voltage relaxation model is developed from experimental investigation of the relationship between the open-circuit time and the relaxation time (i.e., the time constant) of the diffusion RC circuit in the second-order RC model. Based on the new model, the rapid, adaptive and online OCV prediction method is proposed, which ensures that the cell OCV can be predicted quickly and accurately under open-circuit conditions with a low computational complexity. Additionally, the accuracy and universality of the new model and the new OCV prediction method are verified on cells with different cathodes.

2. Experiment design

In this research, 32650-type $LiFePO_4$/graphite cells with a capacity of 5 Ah and 32650-type $LiMn_2O_4$/graphite cells with a capacity of 6 Ah were chosen as the research objects. The tests were performed on single cells and divided into two parts. The first part of the tests aims to examine the cell's OCV behavior of relaxation to develop a new relaxation model. The goal of the second part of the tests is to validate the effects of the new model and the new rapid algorithm.

2.1. Relaxation characteristic test

In this part, in order to study the voltage relaxation behaviors after different working conditions and develop a general voltage relaxation model, six tests from (a) to (f) were performed sequentially with different SOC points, temperatures and charge–discharge schedules. Each test can be divided into two steps: the load step and the relaxation step. During the first step (i.e., load step), the cell works according to one of the six set modes detailed in Table 1. During the second step (i.e., relaxation step), the cell was at rest for 20 h to obtain the static OCV that is taken as a true value. If two neighboring tests have the different working temperatures, another 20 h rest period, at the temperature of the latter test, was needed. Additionally, before the tests, the cell was fully charged to SOC = 1 with constant current–constant voltage (CCCV) (a constant current 0.5 C charge until the voltage reaches the upper limit, followed by a constant voltage charge until the current is below 0.05 C). The experiments of this part were only performed on the $LiFePO_4$ cell.

2.2. Validation test

The test in this part was administered to validate the efficacy of the new model and the rapid OCV algorithm. First, the cell was fully charged by CCCV and then rested for 5 h. Second, the federal urban driving schedule (FUDS) test was administered for 1 h. Finally, following a rest of 20 h, the cell voltage was measured as a true value for OCV. To verify the universality of the rapid OCV prediction algorithm, the validation tests were performed on both the $LiFePO_4$ and $LiMn_2O_4$ cells.

2.3. Measurement equipment

All tests were performed with a channel of the Arbin instruments' BT2000 test bench (18 V, ±100 A), which has a voltage measurement accuracy of ±0.01% and a current measurement accuracy of ±0.02% on the full-scale value. An Agilent 34410A 6½-digit multimeter was used as an auxiliary to measure the voltage; the measurement accuracy of the multimeter is less than 0.1 mV for the cell's voltage. Moreover, the cell ambient temperatures were controlled within ±2 °C by incubators in all tests.

3. Proposed model and method

In this section, the battery relaxation behavior will be studied first. Based on the study, a new relaxation model and the corresponding application method will be discussed.

3.1. Results of the characteristic test

Referring to Section 2.1, corresponding to six characteristic tests from (a) to (f), the curves of the load steps are shown in Fig. 1, and the relaxation processes are shown in Fig. 2. When the battery switches from working to open-circuit state, the cell's actual voltage does not immediately reach the equilibrium state because its internal chemical and mechanical processes do not disappear immediately with the current cutoff. The voltage without full relaxation cannot represent the cell's OCV that coincides with the battery's electro-motive force (EMF) [13]. Herein, the EMF is the voltage measured across the anode and cathode, and equals the

Table 1
The details for the load steps of the characteristic tests from (a) to (f). Herein, the SOCs are measured by a coulomb counting method.

Test	Temperature	Charge–discharge process
(a)	30 °C	Discharge from SOC = 1 to SOC = 0.9 with 2 C
(b)	30 °C	Federal urban driving schedule (FUDS) cycle test from SOC = 0.9 to SOC = 0.7
(c)	50 °C	Discharge from SOC = 0.7 to SOC = 0.4 with 0.5 C
(d)	10 °C	Discharge from SOC = 0.4 to SOC = 0.3 with 0.5 C
(e)	30 °C	Charge from SOC = 0.3 to SOC = 0.5 with 1 C
(f)	30 °C	Charge from SOC = 0.5 to SOC = 0.8 with 0.5 C