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A Capacity Fading Model of Lithium-Ion Battery Cycle Life Based on the Kinetics of Side Reactions for Electric Vehicle Applications

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ABSTRACT

Battery life prediction is one of the critical issues that restrict the development of electric vehicles. Among the typical battery life models, the mechanism model focusing on the internal physical or electrochemical processes has a stronger theoretical foundation and greater accuracy. The empirical formula, which relies on the simplified mechanism, has a concise model structure and more flexibility in vehicle applications. However, the internal aging mechanism rarely correlates with the external operating characteristics.

Based on the summary of the capacity fading mechanism and the reasoning of the internal kinetics of side reactions during the aging process, a lifetime model of the lithium-ion battery is established in this paper. The solutions to the vital parameters based on the external accelerated life testing results are also presented. The testing sample is a manganese oxide lithium-ion battery of 8 Ah. The validation results indicated that the life model established in this paper can describe the capacity fading law of the lithium-ion battery and the operability and accuracy for vehicle applications.

1. Introduction

Research into lithium-ion battery life started in the 1980s with the development of the lithium-ion battery. The selection, grouping, usage, maintaining, and charge–discharge policy of batteries used in EV are all restricted by the battery life. Therefore, battery life prediction technology has become an important issue. Effective battery life prediction can provide guidance for cell grouping and battery use and thus extend the battery life and reduce the cost of the vehicle.

As for the capacity fading of the lithium ion battery, there have been many different methods of battery life modeling for reference, and most of them can be classified into one of the following approaches.

(1) Aging mechanism models, as demonstrated in [1–6], which are usually based on the porous electrode theory [7,8] and nano-mechanics [9,10], describe the electrode process and physical deformation of the specific components within the lithium ion battery, such as the diffusion behavior, SEI generation and lattice distortion. This type of aging mechanism model has the ability to elaborate the internal aging process of the lithium-ion battery.
(2) Empirical formula derived from the external characteristic curve under the given external situation, as demonstrated in [11–13]. The degradation law of the testing samples is presented based on the cycle performance curve or the charge/discharge curve at different life stages, and the simplified lifetime model is established. The lower computing requirements make this model feasible for vehicle application. The parameters and the order of this type of model are usually identified as constant values, which are always an average value of the fitting results obtained from the accelerated tests repeated under different testing conditions.
(3) Data-driven models, such as statistical models, Monte Carlo methods, black models based on the fuzzy reasoning machine, and SVM [14–17]. These types of models are based on the assumption that the aging process is a steady stochastic process over the whole battery life, and the modeling method is more focused on mining the relationship between external excitation and object response rather than the degradation mechanism.

Based on the summary of commonly recognized irreversible capacity fading mechanisms and the side reactions in lithium-ion batteries, especially for manganese oxide lithium-ion batteries, this paper establishes an internal kinetics equation for the simplified

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side reactions during the battery capacity fading process. These kinetics are applicable to the arbitrary chemical reaction order. Through integrating the external impact factors into the related parameters of the kinetics equation, a theoretical battery lifetime model, combined with the influence of the external impact factors, is established, and the detailed mathematic reasoning is presented concurrently. The reasoning process has shown that our model is scalable by adding additional external factors into the model when necessary. The order of the use time is not emphasized because the parameters in our model are not fixed, which can be solved by interpolation tables established by accelerated life testing results. Because it is difficult to measure the concentration of lithium ions in vehicle applications, which is a required parameter in the life model, the life model needs a pre-specified reference operating condition. Although the testing sample is the high-power manganese oxide lithium-ion battery, the whole life modeling method is also applicable to other types of batteries under the condition that the other types have similar capacity fading mechanisms. The comparison between the cycle life of the actual testing sample and the prediction results of the battery lifetime model has shown that the model can reflect the irreversible capacity loss trend of the lithium-ion battery.

This paper is divided into 5 sections. Section 1 reviews the status quo of battery life evaluation. In section 2, the detailed accelerated life experiments are presented. The core of the paper, including the summary of the aging mechanism, the kinetic equation of the aging process, the capacity fading model and the solution of the critical parameters, are presented in section 3 in detail. Section 4 analyzes the testing results of the accelerated life testing and proposes a simplified solution of the critical parameters for our testing samples. The actual values of these parameters will also be obtained simultaneously in this section. Combining the concrete parameters with the cycle life model established in section 3, section 4 constructs the life model for our battery sample and verifies the accuracy of the model. Finally, several conclusions will be presented in section 5.

The abbreviation of the glossary used in this paper is listed in Table 1.

Table 1
Glossary of terms.

Note	Meaning
CC	Constant current
CV	Constant voltage
T	Ambient temperature
I	Discharge current rate
SEI	Solid Electrolyte Interface
Mi	Substance i can be reacted with lithium ion
C_{Li+}	Concentration of the active lithium ion
t	Usage time
k	Reaction rate constant
n	Reaction order
K	Boltzmann constant
H	Planck constant
R	Molar gas constant
A	Pre-exponential factor
E_a	Activation energy
$c^{\ominus}$	Standard concentration
$\Delta \neq s^{\ominus}$	Standard activation entropy
ΔS	Activation entropy
ΔQ	Electrochemical Peltier heat
$\Delta \neq Q^{\ominus}$	Standard electrochemical Peltier heat
e_i	External impact factor i
M	Variable related to C_{Li+}
M_0	Value of M corresponding to the initial state
ΔM_0	Change value of M corresponding to the initial state
dM/dt	Change rate of M
$k^{/}$	Variable related to n
L	Cycle number
dr	Transient fading rate of capacity
Δr	Fading rate of capacity relative to a certain life state
Δr_0	Fading rate of capacity relative to initial state
Q_{Σ}	Accumulated electricity
C_{Qt}	Actual capacity of the lithium-ion battery at a certain life state
C_{Q0}	Initial capacity of the lithium-ion battery
ΔT	Discharge time within one cycle for a specified operating condition
f(I,DoD)	Function indicating the influence of the discharge rate and DoD

2. Experimental

The sample used in the battery life experiment is a high-power manganese oxide lithium-ion battery with a rated capacity of 8 Ah supplied by cooperating enterprises. Ruling out the abusing factors, it is generally accepted that the external factors affecting lithium-ion battery life include T, I and DoD [11], where the value of DoD is relative to the fully charged state due to the constraints of experimental devices.

The tests in this paper are composed of accelerated cycle life tests and model validation tests; the testing matrices for the accelerated life test also can be used to study the impact mode of the external factors on battery performance. The performance calibration test will be imposed after the specified cycle number, as well as at the initial state.

In the performance calibration test, the cycle life test and the validation test, we charge the battery with the CC-CV mode. The charge rate in the CC stage is 1/2 C, and the cut-off voltage is 4.2 V. The cut-off current is set to 1/100 C in the CV stage, and the three steps all proceed at 25°C ambient temperature.

In the performance calibration test, we discharge the battery with the CC mode; the discharge rate is 1/2 C, and the cut-off voltage is 2.7 V. The testing temperature is set to 25°C.

In the cycle life test, we discharge the battery with CC mode. The cut-off voltage is 2.7 V. T, I, DoD and the corresponding steps between each calibration test under different accelerated life test situations are listed in Tables 2 and 4. In addition to obtaining the results of the cycle life test, these tests can also be used to compare the impact character of different external factors. Table 2-Table 4 depict the accelerated effects of T, I, and DoD on battery performance.

Table 2
The testing of the temperature impact on the battery capacity degradation.

Test No.	T(°C)	I(C)	DoD(%)	Sampling interval
1	20	1	100	70
2	30	1	100	60
3	40	1	100	30
4	50	1	100	30

For normalization of our experimental results, we chose a T of 40°C and I of 1 C and DoD of 100% as the reference operating conditions. The model prediction accuracy can be verified by the testing results of the arbitrary operating conditions, and our choice is listed in Table 5.

Taking the inconsistence between individual cells into account, every testing item is repeated three times. When we evaluate the battery life state under a specific operating condition, we use the average value of the three samples. However, due to the calendar

Table 3
The testing of the discharge rate impact on the battery capacity degradation.

Test No.	T(°C)	I(C)	DoD(%)	Sampling interval
1	40	1	100	30
2	40	2	100	30
3	40	3	100	20
4	40	4	100	20
5	40	5	100	15