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## Degradation Predictions of Lithium Iron Phosphate Battery

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### Abstract

Degradation mechanisms of lithium iron phosphate battery have been analyzed with calendar tests and cycle tests. To quantify capacity loss with the life prediction equation, it is seen from the aspect of separating the total capacity loss into calendar capacity and real cycle capacity loss. The real cycle capacity loss of total capacity loss was derived by subtracting the calendar capacity loss parts during cycle tests. It is considered that calendar capacity loss is dominated by SEI formation. On the other hand, real cycle capacity loss includes structure disorder of electrodes and promotion of SEI growth such as delamination and regrowth. Generally, the test results indicated that capacity loss increases under high temperature and SOC condition, and SOC range ( $\Delta$ SOC) is not related to the loss. However, we founded that the test results under 5°C condition do not exactly show the same tendency of degradation. As a result, the life prediction equation is based on the chemical kinetics and it can only be adopted only beyond the 15°C temperature limitation. At this time in life prediction equation, to take  $\Delta$ SOC into consideration and describe the real cycle capacity loss specifically with amounts of lithium-ion intercalation/deintercalation, the processing amount of current is adopted as the standard of capacity degradation instead of the cycle number. Finally, it is considered to be possible that certain reactions such as further structure disorder or lithium plating caused under low temperature. However, we also founded that DC internal resistance tests results indicated that only calendar capacity loss can apply to chemical kinetics. It is necessary to consider the other construction method of the life prediction equation in the future.

*Keywords: lithium-ion battery, durability, degradation prediction, lithium iron phosphate battery, BEV (Battery Electric Vehicle)*

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### 1 Introduction

In order to clarify the degradation characteristic of lithium-ion battery for battery electric vehicle (BEV), our research group conducting calendar capacity loss tests and cycle capacity loss tests

mainly to original developed Lithium iron phosphate battery. Until now, we analysed influence of temperature and SOC. As a result, it was clear to inhibit drastically the degradation by change the operation of the SOC range at actual running for BEV [1]. Degradation factors of

lithium-ion batteries have been reported by previous researches [2] [3] [4]. It is considered that dominated by SEI (solid electrolyte interface) formation at negative electrode and structure disorder of electrodes with lithium-ion intercalation/deintercalation.

In this paper, in order to investigate the influence of the cycle capacity loss, tests were conducted with the middle of the processing SOC with different  $\Delta$ SOC. Also, analysed the influence of current at real cycle capacity loss and the factor of DC internal resistance.

## 2 Evaluation Tests

### 2.1 Test battery cell

Figure 1 and Table 1 show the specification of the test battery cell. Lithium iron phosphate battery is known for its superiority of safety and the cost of manufacturing. The test battery cell is a laminate type cell which has superior rapid charging performance.



Figure 1: Test battery cell

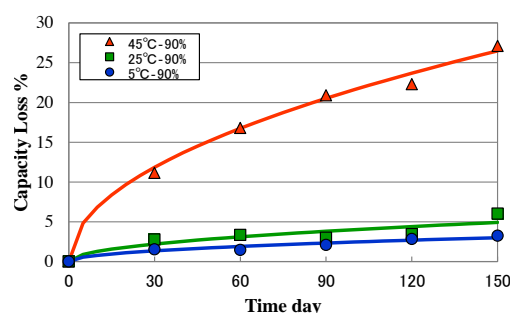
Table 1: Test battery specification

Cathode Material	LiFePO <sub>4</sub>
Anode Material	C <sub>6</sub> (Graphite)
Rated Voltage	3.25 V
Rated Capacity	6.2 Ah
Dimensions (mm)	L120×W3×H140

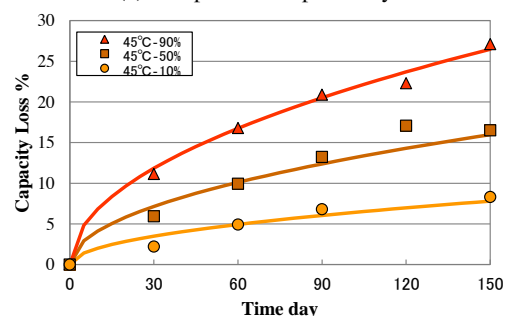
### 2.2 Calendar capacity loss tests

Parameters of the calendar capacity loss tests are temperature (5 °C, 25 °C, 45 °C) and SOC (10%, 50%, 90%). The capacity was checked about every 30 days and it is followed the conditions below: EOCV of 4.0 V, end of discharge voltage (i.e. cut off volt-age) of 2.0 V, CC-CV charge protocol with CV process for 5 minutes, discharging rate of 1C and charging rate of 1/2C, under 25 °C ambient temperature.

Figure 2 shows the results of the calendar capacity loss tests. These results indicated that the capacity loss increased under high temperature and high SOC condition. It progresses linearly with the square root of the time. It is considered that the main cause is the reaction between lithium-ion and electrolyte which is called SEI formation is accelerated under these conditions. As a result, the amounts of reversible lithium-ion during charging process which is related to the capacity of the battery decreases as the SEI formed.



(a) Temperature dependency



(b) SOC dependency

Figure 2: Results of calendar capacity loss tests

### 2.3 Cycle capacity loss tests

Table 2 shows the condition of cycle capacity loss tests with parameters of  $\Delta$ SOC (10%, 20%, 50%) and temperature (5 °C, 15 °C, 25 °C) which is to confirmed the capacity fading below room temperature 25 °C and the influence of SOC range.

Table 2: Cycle test condition ( $\Delta$ SOC)

Temperature	5 °C, 15 °C, 25 °C	
$\Delta$ SOC	50%, 20%, 10%	
Charge/Discharge Amount (/cycle)	$\Delta$ SOC=10%	0.620Ah/0.620Ah
	$\Delta$ SOC=20%	1.24Ah/1.24Ah
	$\Delta$ SOC=50%	3.10Ah/3.10Ah

The study of variation of SOC range, which is also called DOD (depth of discharge), have been reported by previous researches [5] [6]. All of cycle tests of these studies are started from SOC = 100% with different depth of the discharge amount of current. However, since the test condition includes the degradation of high voltage usage, it is hard to clarify the influence of SOC range.

In this paper, these tests are identical with SOC 60% as the middle of the processing SOC with different  $\Delta$ SOC. To exclude the effect of high voltage usage, maximum of  $\Delta$ SOC of the tests is 50% which remains the SOC between 30% and 80%. Figure 3 shows the difference between cycle tests with the parameter of  $\Delta$ SOC which are mentioned.

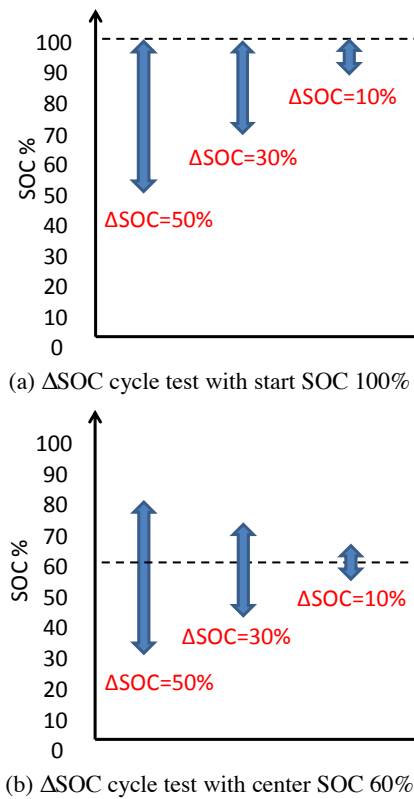


Figure 3: Different test conditions with parameter of  $\Delta$ SOC

Figure 4 shows the result of the cycle capacity loss tests. This result indicated that the capacity loss increased under high  $\Delta$ SOC condition. However, these amount of processing current and time are different at 1 cycle. Therefore, each result occur difference. Also indicated that the capacity loss of  $\Delta$ SOC 50% were higher than  $\Delta$ SOC 10% and  $\Delta$ SOC 20%.

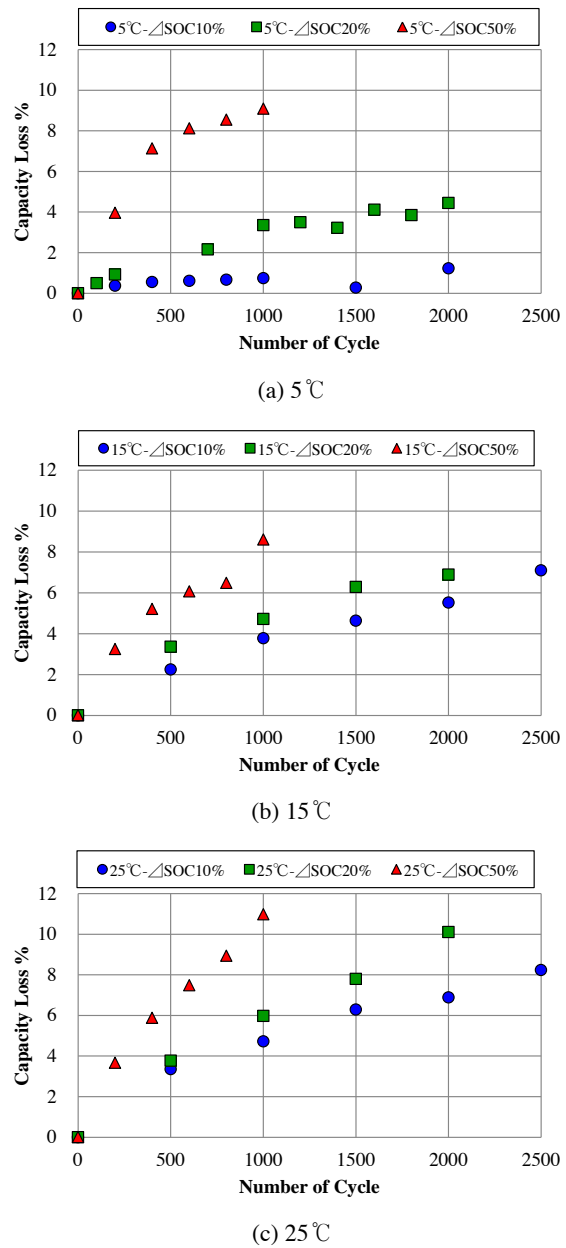


Figure 4: Result of cycle capacity loss tests

## 2.4 DC internal resistance tests

Figure 5 shows the method of DC internal resistance tests. The tests conduct with the following procedure.

- I. Get the terminal voltage  $V_0$  at equilibrium state (25 °C, SOC 50%).
- II. Apply the current  $I=2.067A$  (about 1/3C of capacity) for 10 seconds and get the terminal voltage  $V_1$ .
- III. Calculate DC internal resistance from  $V_0$  and  $V_1$ .

$$R_{\text{Charge}} = \frac{V_1 - V_0}{I} \quad (1)$$

At DC internal resistance tests for discharge, apply the discharge current for 10 seconds and get the terminal voltage  $V_2$ .

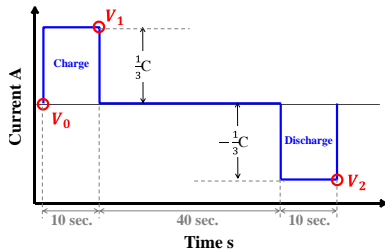


Figure 5: DC internal resistance test

Figure 6 and 7 show the results of the DC internal resistance tests which apply the discharge current on calendar capacity loss tests and cycle capacity loss tests. These results indicated that the DC internal resistance is increasing tendency at the calendar capacity loss tests and no increasing at the cycle capacity loss tests.

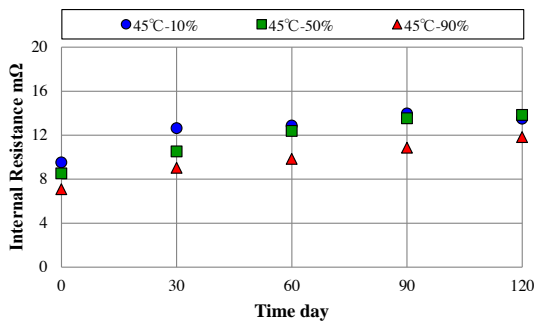


Figure 6: Result of DC internal resistance tests (calendar capacity loss tests)

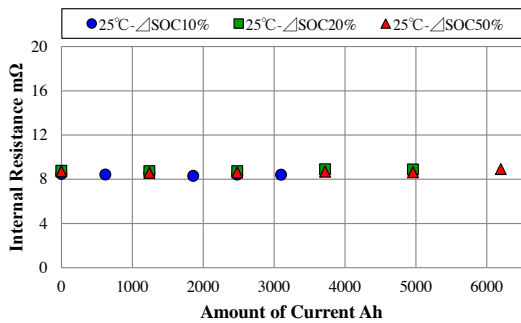


Figure 7: Result of DC internal resistance tests (cycle capacity loss tests)

### 3 Discussion

#### 3.1 Influence of current at cycle capacity loss tests

At cycle capacity loss tests with parameter of  $\Delta SOC$ , it is different amount of processing current and time among each condition. In order to observe the exact influence of the capacity loss, it needs to change horizontal axis from number of cycle to the accumulated current, which means the total amount of charge and discharge current, as Figure 8.

Figure 8 shows the result of the cycle capacity loss tests represented by the accumulated current. These results indicated that that variation of  $\Delta SOC$  is not related to the capacity loss except  $5^\circ\text{C}$ . It can infer that some extra degradation mechanism has caused under low temperature such as lithium plating, or further structure disorder.

#### 3.2 Calculation of real cycle capacity loss

The calendar capacity loss part is considered to be included among cycle capacity loss tests. The real cycle capacity loss characteristic was derived by subtracting the calendar capacity loss during the cycle test from the total capacity loss among cycle tests. In this paper, equation of the calendar capacity loss were quantified with the equation (2) which was derived at conventional our research.

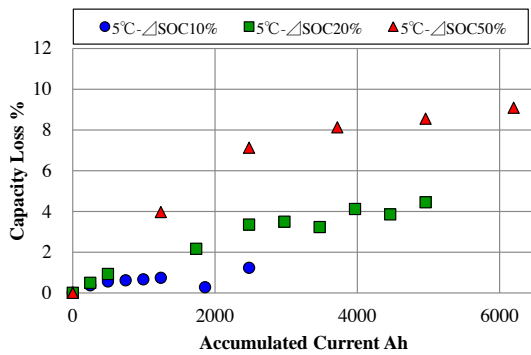
$$\begin{cases} \text{Deduction coefficient of} \\ \text{calendar capacity loss \%} = k_s * t^{0.5} \\ k_s = 4475 * (SOC) * \exp\left(-\frac{49767 - 811V}{RT}\right) \end{cases} \quad (2)$$

Figure 9 shows the real capacity loss with parameters of  $\Delta SOC$ , and the discharging amount is considered to be appropriate as a comparison standard. Generally, it is indicated that  $\Delta SOC$  has no influence on capacity fading.

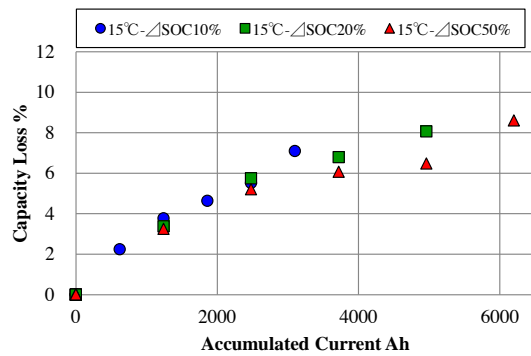
The distinction between calendar capacity loss tests and cycle capacity loss tests is that lithium-ion intercalation/deintercalation of the electrodes. Therefore, processing amounts of lithium-ion during cycle tests, which can be represented by the accumulated current, is considered that it is proper and specific to describe the real cycle loss. Characteristics of real cycle capacity loss were quantified with the equation (3) which is also based on the chemical kinetics. However, the results of the tests also show that the fading

mechanism under 5 °C during the cycle test cannot be generalized by the same way with 25 °C, 45 °C. Therefore, this equation should be limited with the temperature which is above 15 °C.

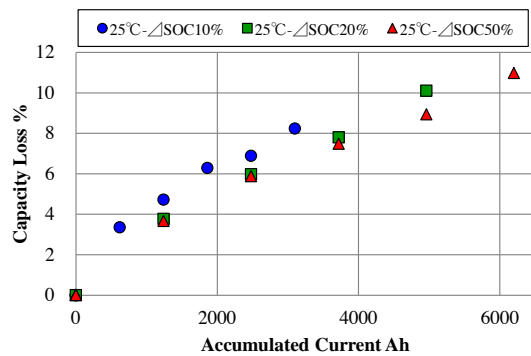
$$\left\{ \begin{array}{l} \text{Deduction coefficient of} \\ \text{cycle capacity loss } \% = k_c * Ah^{0.5} \\ k_c = 1.725 * 10^{-2} (SOC) * \exp\left(-\frac{5890 - 0.1012V}{RT}\right) \end{array} \right. (3)$$



(a) 5 °C



(b) 15 °C



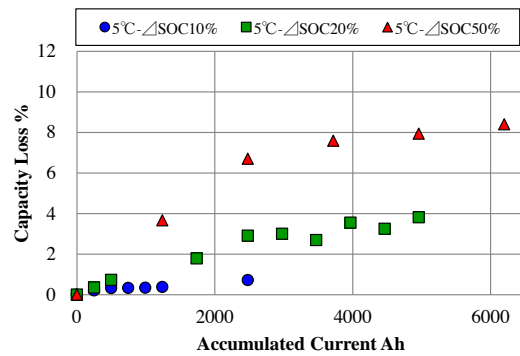
(c) 25 °C

Figure 8: Result of cycle capacity loss tests (current Ah dependency)

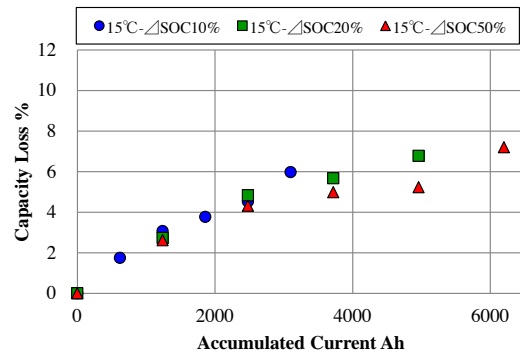
### 3.3 Factorial analysis of DC internal resistance

In order to investigate the transition of DC internal resistance in detail, the rate of increase at the calendar capacity loss tests are evaluated.

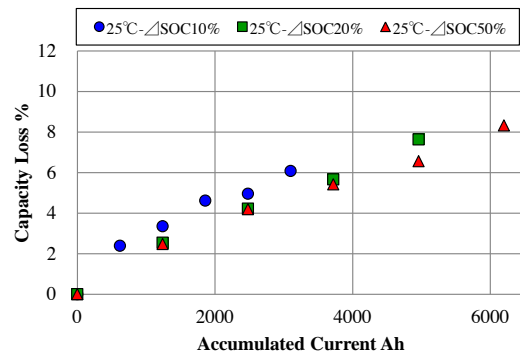
Figure 10 shows the rate of increase for DC internal resistance at the calendar capacity loss tests. As a result, the rate of increase progresses linearly with the square root of the time. Also, the result indicated that the increase promote under high SOC condition. Therefore, the DC internal resistance are dominant in SEI at the calendar capacity loss and not at the cycle capacity loss.



(a) 5 °C



(b) 15 °C



(c) 25 °C

Figure 9: Real cycle capacity loss test

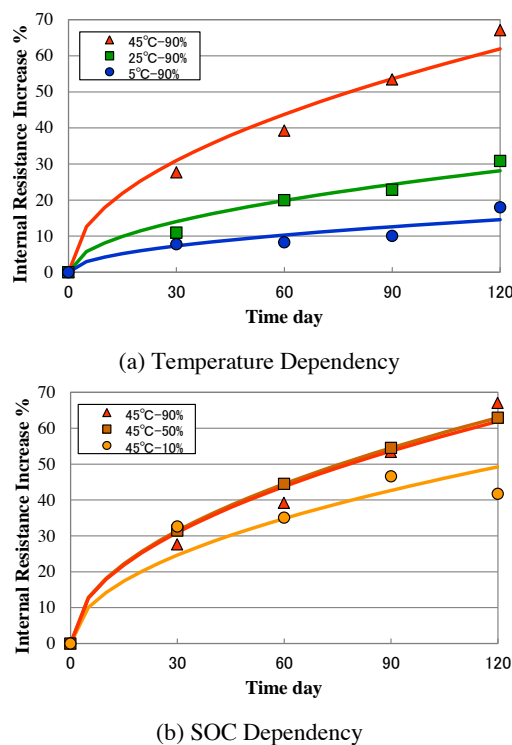


Figure 10: Rate of Increase for DC Internal Resistance at Calendar Capacity Loss

## 4 Conclusion

In order to clarify the degradation characteristic of lithium-ion battery for BEV, our research group conducted calendar capacity loss tests, cycle capacity loss tests and DC internal resistance tests to original developed Lithium iron phosphate battery. The results are as follows:

(a) The calendar capacity loss progresses linearly with the square root of the time. It increased under high temperature and high SOC condition. Battery capacity degraded 27% during 150days with 45 °C, SOC 90%.

(b) The cycle capacity loss progresses with the number of cycle. At real cycle capacity loss, battery capacity degradation promotes under high  $\Delta$ SOC and it progresses linearly with the square root of the accumulated current. However, the fading mechanism under 5 °C cannot be generalized by the same way with 25 °C, 45 °C.

(c) The DC internal resistance progresses linearly with the square root of the time at the calendar

capacity loss. Also, it was no increasing at the cycle capacity loss.

(d) Therefore, the DC internal resistance are dominant in SEI at the calendar capacity loss and not at the cycle capacity loss. It is necessary to consider the other construction method of the life prediction equation in the future.

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