Verification of Life Estimation Model for Space Lithium-Ion Cells

Hiroaki Yoshida, a, * Nobutaka Imamura, a Takefumi Inoue, a Koichi Takeda, a and Hitoshi Naito b

a Large Lithium-ion Engineering Dept., Special/Lithium Battery Div. GS Yuasa Technology Ltd. (Nishinoshio Kishihon, Minami-ku, Kyoto 601-8520, Japan)

b Space Power Systems Group, Aerospace Research and Development Directorate Japan Aerospace Exploration Agency (Tsukuba, Ibaraki 305-8505, Japan)

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Large capacity Li-ion cells with 100 Ah for satellite application had been developed in 1999, and calendar and cycle life characteristics of the cells had been evaluated under various test conditions with wide range of temperature (0 °C – 60 °C), depth of discharge (3% – 80% DOD), and state of charge (0% – 100% SOC). These tests were started in 1999, and the data have been accumulated until 2008 for around ten years. From these results, we have confirmed that GYT Space Li-ion cells have sufficient capability to achieve the mission life requirements for several kinds of artificial satellites. Furthermore, we have discovered that our simple life estimation model needs to be modified to consider SEI growth blocking mechanism. It means that the SEI growth is blocked by the adjacent SEI layers, therefore calendar capacity loss is affected by not only its test term, temperature, and state of charge but also its calendar capacity loss values. Our modified estimation formula is that a rate of calendar capacity loss is decreased in proportion to the 2.4th power of the calendar capacity retention. By using the modified formula, the estimation results show very good fitting with the long term cell test data for ten years.

Key Words: Lithium-Ion Cell, Life Estimation Model, Calendar Capacity Loss, Artificial Satellite

1 Introduction

Large Li-ion cells are widely used as a main power source for deep sea investigation vehicles, auto guided vehicles (AGVs), EVs, rockets and artificial satellites because the cells are lighter in mass and smaller in size compared with other kinds of secondary cells. 1,2 The artificial satellites generate electric power by solar panels during sunshine period and the surplus energy is charged to the secondary cells. On the other hand, the cells supply the satellite with the electricity during eclipse period. The general performance demand of geo-stationary orbit satellites (GEOs) at an attitude of 36,000 km is a cycle life of 1.500 cycles at an average 56% (max. 70%) DOD for eclipse season and a calendar life of 18 years (3 years ground storage + 15 years in orbit); that of low earth orbit satellites (LEOs) at an attitude of less than 1,000 km is a cycle life of 40,000 cycles at 25% DOD and a calendar life of 11 years (3 years ground storage + 8 years in orbit).

Regarding calendar life characteristics, satellite makers require 18 years life for the Li-ion cells. The real time evaluation needs unimaginable test period, therefore we had thought out simple capacity loss mechanism and life estimation method for the Li-ion cells. 3 The evaluation test using 65 Space Li-ion cells with 100 Ah was started in June 1999. The cells have been evaluated under the test conditions with wide range of temperature (0 °C – 60 °C), depth of discharge (3% – 80% DOD), and state of charge (0% – 100% SOC), 4,5 and the test data have been accumulated for around ten years. From these test results, we have confirmed that GYT Space Li-ion cells have sufficient capability to achieve the mission life requirements for several kinds of artificial satellite such as GEOs and LEOs. Furthermore, we have discovered that our simple life estimation model based on our capacity loss mechanism needs to be modified to consider Solid Electrolyte Interface (SEI) growth blocking mechanism. It means that the SEI growth is blocked by the adjacent SEI layers, therefore calendar capacity loss is affected by not only its test term, temperature, and state of charge but also its calendar capacity loss values. Our modified estimation formula is that a rate of calendar capacity loss is in proportion to the 2.4th power of the calendar capacity retention. By using the modified formula, we have confirmed that the estimation results show very good fitting with the long term cell test data for ten years.

In this paper, we focus on our modified capacity loss mechanism and accurate life estimation method for the Space Li-ion cells, and describe the accumulated calendar and cycle life test data and the cell life estimation results under the conditions of practical GEOs and LEOs missions.

2 Experimental

2.1 Test cell

Elliptic cylindrical 100 Ah cells for space applications have been used for this study. The cell element has an elliptic cylindrical shape of spiral construction where the positive and negative electrodes are wound together.
with micro porous separators. The positive electrode uses lithium cobalt dioxide (LiCoO$_2$) and the negative electrode uses carbon materials. All elements are tightly enclosed in an elliptical cylindrical aluminum-alloy container, which has rupture plates and hermetically sealed terminals. After filling with the electrolyte, the opening of the cell case is laser welded to keep its air tight in space. The electrolyte is a mixture of alkyl carbonate solvents and a Li salt. Table 1 shows the specifications of the 100 Ah Li-ion cells. The capacity of 100 Ah can be obtained at a maximum charge voltage of 3.98 V. The lower end of charge voltage has made it possible for the cells to have a long life.

### 2.2 Capacity loss mechanism

Capacity loss mechanism for Space Li-ion cell is described in our previous paper in 2003.\textsuperscript{3} We are assuming the following two mechanisms are major causes of the capacity loss. One is calendar capacity loss and the other is true cycle capacity loss.

The calendar capacity loss is caused by consumption of Li-ions in a negative electrode. The negative electrode such as Lithium-graphite intercalated compounds react with electrolyte very easily, and then the reaction forms SEI layer between the negative electrode and the electrolyte. It is generally speaking that the SEI is made of Li-ions in the negative electrode and the electrolyte. The Li-ions in the negative electrode is active material of the cell, therefore the progress of the SEI formation, means increasing in capacity loss of the Li-ion cell.

On the other hand the formed SEI layer obstructs the progress of the reaction because solvent molecules have to pass through the SEI layer to react with Li-ions in a negative electrode; therefore it can be assumed that the reaction rate is in inverse proportional to the thickness of the SEI layer. When thickness of SEI layer corresponds to amount of consumed Li-ions (amount of calendar capacity loss), the following equation (1) was derived.

$$\text{Amount of calendar capacity loss} / \% = k_f \times t^{1/2} \quad (1)$$

The calendar capacity loss is proportional to square root of time, and we predicted that the rate constant $k_f$ is affected by temperature and SOC. On the basis of this mechanism, we planned evaluation test matrix using 32 Li-ion cells with 100 Ah to obtain the $k_f$ values focusing on effect of temperature and SOC.

Regarding the true cycle capacity loss, we assume that it is caused by mechanical stress of positive active material particles during charge-discharge cycles. The electrode is composed of current collector, active material particles, electron conductor, and plastic binder. Active material particles expand during charging, and shrink during discharging. The repeat of change in volume degrades electron paths in the electrode and it generates isolated active material particles from electron conductive network. We had experimentally confirmed that the true cycle capacity loss is in proportional to square root of charge-discharge number of cycles. The true cycle capacity loss can be expressed by formula (2).

$$\text{Amount of true cycle capacity loss} / \% = k_c \times N^{1/2} \quad (2)$$

Where $N$ is charge-discharge cycle number and $k_c$ is a rate constant corresponding to the mechanical reaction. This formula means the effect of volume change of the active material on the electron path degradation is large at the beginning of life (BOL), after that the effect gradually decreases as the cycle progress. The mechanism can be imagined as shown as follows. The electrode is closely packed when the cell is manufactured, therefore the electrode is prone to loose at the BOL and it causes the degradation of electron path. As the cycle progress, some space is formed in the electrode and it works as buffer against the active material volume change. As the result, degradation becomes small.

On the basis of this mechanism, we planned evaluation test matrix using 32 Li-ion cells with 100 Ah to obtain the $k_c$ values focusing on effect of temperature and DOD, and we had reported that the rate constant $k_c$ is not affected by temperature from 15°C to 60°C.

From this investigation, we clarified the effect of temperature and SOC on rate constant $k_f$ and the effect of DOD on rate constant $k_c$. Finally we had reported that capacity retention of Li-ion cells on any conditions can be calculated by using formula (1), (2) and (3).

$$\text{Capacity retention of Li-ion cells} / \% =$$

$$\text{100−calendar capacity loss} / \% −$$

$$\text{true cycle capacity loss} / \% \quad (3)$$

### 2.3 Calendar and cycle life tests

On the basis of the capacity loss mechanism, we presume the calendar and true cycle capacity loss can be evaluated individually. Table 2 shows calendar life test matrix using 32 Li-ion cells with 100 Ah. The test has been performed at various conditions to evaluate the effect of temperature and SOC on the rate constant $k_f$ during storage. A matrix test of four temperatures (60°C, 35°C, 15°C, and 0°C) and five SOCs (100%, 80%, 60%, 30%, 5%) was performed. Terminal voltage and temperature of the test cells were kept at the specified values as shown in Table 2, and capacities of the cells were
checked every month. By definition, calendar capacity loss is progress of permanent capacity loss during non-operation period, and the evaluation should be performed under open circuit condition. However, we performed it under float charging condition to remove a factor of change in SOC during the test period caused by self-discharge of cells.

Table 3 and 4 show cycle life test matrix using 33 Li-ion cells with 100 Ah. The test has been performed at various conditions to evaluate the effect of temperature and DOD on the rate constant k<sub>c</sub> and the multiplier on the cycle number. A matrix test of four temperatures (60°C, 35°C, 15°C, and 0°C) and five DODs (80%, 50%, 25%, 10%, and 3%) was performed.

All the tests were performed using FUJITSU DENSO charge-discharge testing system (max. current: 100 A, voltage accuracy: ± 4 mV, current accuracy: ± 40 mA) and NAGANO SCIENCE temperature chamber CH40-15P (temperature accuracy: ± 1°C).

### Table 3 Charge-discharge cycle life test matrix using 33 Li-ion cells with 100 Ah.

<table>
<thead>
<tr>
<th>Temperature/ ºC</th>
<th>SOC/float charging voltage</th>
<th>DOD/33%</th>
<th>DOD/50%</th>
<th>DOD/25%</th>
<th>DOD/10%</th>
<th>DOD/3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1 cell 1 cell 1 cell 1 cell 1 cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>2 cells 2 cells 2 cells 2 cells 2 cells</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1 cell 2 cells 5 cells *2 cells 2 cells</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1 cell 1 cell 1 cell 1 cell 1 cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*For confirmation of dispersion.

### Table 4 Test Conditions for charge-discharge cycle life test matrix.

<table>
<thead>
<tr>
<th>DOD/%</th>
<th>Charge condition</th>
<th>Discharge condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Constant current value/</td>
<td>Constant voltage value/</td>
</tr>
<tr>
<td></td>
<td>total time</td>
<td>Discharge condition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Discharge time</td>
</tr>
<tr>
<td>80</td>
<td>50 A/3.98 V/3.6 h</td>
<td>50 A/1.6 h</td>
</tr>
<tr>
<td>50</td>
<td>50 A/3.98 V/3.0 h</td>
<td>50 A/1.0 h</td>
</tr>
<tr>
<td>25</td>
<td>50 A/3.98 V/0.5 h</td>
<td>50 A/0.5 h</td>
</tr>
<tr>
<td>10</td>
<td>50 A/3.98 V/0.22 h</td>
<td>50 A/0.2 h</td>
</tr>
<tr>
<td>3</td>
<td>50 A/3.98 V/0.066 h</td>
<td>50 A/0.06 h</td>
</tr>
</tbody>
</table>

*Capacity check condition:
Charge: 20 A to 3.98 V followed by a constant voltage of 3.98 V for a total of 8 hours at 15°C.
Discharge: 20 A to 2.75 V at 15°C.

### 2.4 Evaluation test for actual satellite usage condition

#### 2.4.1 LEO simulation test (real time)
Five Li-ion cells with 100 Ah have been tested by the following LEO simulated conditions. The purpose of this test is to verify our Li-ion cell life performance, and to confirm our estimation method accuracy by comparing the estimation and the test results. The capacity check was performed every 5,000 cycles. The test equipment is the same as the ones that are used for calendar and cycle life test.

**Charge-discharge cycle condition:**
Charge: 30 A to 3.95 V followed by a constant voltage of 3.95 V for a total of 1.0 hours at 15°C.
Discharge: 50 A for 0.5 hours at 15°C.

**Capacity check condition:**
Charge: 10 A to 3.95 V followed by a constant voltage of 3.95 V for a total of 16 hours at 15°C.
Discharge: 50 A to 3.00 V at 15°C.

#### 2.4.2 GEO simulation test (partially acceleration)
Two Li-ion cells with 100 Ah have been tested by the following GEO simulated conditions. GEO satellites go into eclipse season twice a year. The season consists of 42 days and the centers of the seasons are Vernal Equinox Day and Autumnal Equinox Day, respectively. The other 140 days per a half-year is solstice season and the satellite is in sunshine all day, therefore the cells stand at charged condition. In this test, temperature acceleration test has been performed in substitution for the solstice season, the 140 day at 0°C is shorten to 8 days at 25°C. The temperature acceleration ratio was derived value from the calendar life test matrix data. During the test, capacities of the test cells were checked every season by the following conditions. The test equipment is the same as the ones that are used for calendar and cycle life test.

**Charge-discharge cycle condition (max. 70% DOD, average 56% DOD):**

**< Eclipse season: 42 days / season >**
Charge: 10 A to 3.98 V followed by a constant voltage of 3.98 V for a total of 12 hours at 15°C.
Discharge: 58 A for max. 72 min. (ave. 58 min.) at 15°C.
Rest: Around 11 hours (12 hours – discharge time)

**< Accelerated solstice season: 8 days / season >**
Stored at 50% SOC for 8 days at 25 deg.C

**Capacity check condition:**
Charge: 10 A to 3.98 V followed by a constant voltage of 3.98 V for a total of 20 hours at 15°C.
Discharge: 58 A to 2.75 V at 15°C.

### 3 Results and Discussion

#### 3.1 Calendar life test
Figure 1 shows changes in discharge capacity retention of the 100Ah cells on the calendar life test at 100%, 60%, and 5% SOC for around ten years. The capacity loss at high temperature of 60°C and 35°C becomes very large, and the rate of capacity loss gradually becomes small as the progress of time. On the basis of our con-
Fig. 1 Changes in discharge capacity retention of 100 Ah Li-ion cells at (a) 100% SOC, (b) 60% SOC, and (c) 5% SOC.

Conventional capacity loss mechanism in 2003, we estimated that the calendar capacity loss is in proportional to square root of time.

Figure 2 shows changes in discharge capacity retention of the 100 Ah cells at 60% SOC, and the horizontal axis is changed to square root of time. The test data at 0°C and 15°C shows good fitting to the straight line, but both 35°C and 60°C data is getting out of the line as the time progress. The test data shows a tendency to restrain progress of capacity loss as increasing in amount of calendar capacity loss.

The test results suppose us that there is SEI growth blocking phenomenon as the progress of the reaction. SEI growth model proposed in 2003 was considered only thickness of SEI layer and three-dimensional limitation against the growth was not considered. Actual negative electrode is closely packed when the cell is manufactured; therefore the carbon particles contact each other in the electrode as shown in Fig. 3. When the thickness of SEI layer is thin, the dimensional limitation in the electrode is small; however, the reaction is gradually blocked by the adjacent SEI layers in proportion to the progress of SEI growth.

Based on this mechanism, we have thought out a SEI blocking parameter by using the test result and original capacity loss model. The additional parameter affects the rate constant k according to the amount of calendar capacity loss, and formula (4) is derived experimentally.

\[
\text{SEI growth blocking parameter} = \left(1 - \text{amount of calendar capacity loss}\right)^x \quad (4)
\]

Figure 4 shows comparison between calendar life test data of 100 Ah Li-ion cells at 60% SOC and its estimation curves using the SEI growth blocking parameters. X values in \(1 - \text{amount of calendar capacity loss}^x\) were confirmed at 1.0, 2.0 and 3.0 respectively, and we found out suitable X value exists between 2.0 and 3.0. Figure 5 shows comparison between the test data and its estima-
tion curve using the SEI growth blocking parameter of $X = 2.4$. The calendar capacity loss value can be calculated with formula (1) and following modified rate constant formula (5).

$$kf = k_{f_0} (1 - \text{amount of calendar capacity loss})^{2.4} \quad (5)$$

Where $k_{f_0}$ is calendar capacity loss rate constant at BOL.

By using the modified formula, we have confirmed that the estimation results show very good fitting with the long term cell test data from $0°C$ to $60°C$ for ten years.

Calendar capacity loss is affected by not only its test term, temperature, and state of charge but also amount of calendar capacity loss as described above. Based on our test data, we have found out an additional estimation formula that is a rate of calendar capacity loss is decreased in proportion to the 2.4th power of amount of calendar capacity retention.

Figure 6 shows correlation between calendar capacity loss value and SEI growth blocking parameter ($(1-\text{amount of calendar capacity loss})^2$). When the calendar
capacity loss becomes 25% of the initial capacity the SEI growth rate is reduced around half of the initial value.

Figure 7 shows Arrhenius plot of the rate constant $k_f$. The value is calculated from test data for ten years and the calendar capacity loss formula (1) with modified rate constant formula (5). The rate constant $k_f$ is strongly affected by temperature and shows good fitting on a straight line at various SOC. Therefore it is confirmed that the calendar capacity loss is caused by a single chemical reaction, and the activation energy of 43 kJ mol$^{-1}$ to 48 kJ mol$^{-1}$ are derived from slopes of the straight lines in the figure. The negative electrode such as lithium-graphite intercalated compounds reacts with electrolyte very easily; therefore we estimate that this large activation barrier is migration energy for electrolyte solvents in SEI layer.

Regarding the large activation energy for Li-ion cell chemistry, Dr. Abe and Dr. Ogumi studied the charge transfer reaction at electrode/electrolyte interface and reported that the activation energy is 53 kJ mol$^{-1}$ to 59 kJ mol$^{-1}$ at HOPG (highly oriented pyrolytic graphite)/electrolyte interface in 1M- LiClO$_4$/EC+DEC (1:1) electrolyte system. By their theoretical calculation, the activation barrier was found out to be correlated with the interaction between a Li-ion and solvents, and therefore the activation barrier is principally due to the desolvation process of the Li-ion in the electrolyte. The large activation energy of desolvation process shows nearly value against our experimental result of calendar capacity loss (SEI growth) reaction, therefore there is a possibility that calendar capacity loss reaction is limited by the desolvation process of Li-ions too. Electrolyte is composed of aprotic solvents and Li-salt, and the solvents are existing following two situations, one is coordinating against Li-ions and the other is incorporated in solvent structure. Generally speaking, the solvent structure of aprotic organic solvent is not strong such as water molecule structure which is held together by hydrogen-bonding. However, the dipole force of the aprotic organic solvent makes molecular size large and may make solvent transmission in SEI layer difficult. On the other hand, it is thought that generated free solvent molecule size just after the desolvation process is small and can go into the SEI layer easily.

We would like to confirm which process is right by performing additional studies.

3. 2 Cycle life test

Changes in capacity retention of the 100Ah cells at various DOD cycle life test at various temperatures have been accumulated for ten years and verified cycle capacity loss formula (2) with formula (1) and modified rate constant formula (5). As we reported in just before section 3.1, modification of the rate constant $k_f$ is performed in the calendar capacity loss formula, however there is no need to modify our true cycle capacity loss formula (2). Details of the fitting data are described in the following section 3.3.

3. 3 Evaluation test results for actual satellite usage condition

3. 3. 1 LEO simulation test (real time) Figure 8 shows changes in capacity retention of 100 Ah Li-ion cells on 25% DOD LEO real time test at 15°C for eight years at JAXA (Japan Aerospace Exploration Agency). The estimation result is calculated using the calendar capacity loss formula (1) with modified rate constant formula (5) and original true cycle capacity loss formula (2). The estimation curve shows good fitting to the test data. The calculated charge retention after 40,000 cycles at 25% DOD for 8 years is around 70% of the initial capacity. The breakdown in calendar capacity loss 12%, true cycle capacity loss 18%. From this result, we have confirmed that our Space 100 Ah Li-ion cells can operate actual LEO satellite in orbit and the estimation model
has high accuracy.

3. 3. 2 GEO simulated test (partially acceleration) Figure 9 shows changes in capacity retention of 100 Ah Li-ion cells on 70% DOD GEO partially acceleration test and its estimation result. 30 seasons correspond to 15 years operation in orbit. As same as the LEO simulation test, the formulas (1), (5), and (2) are used for the estimation. The estimation curve shows good fitting to the test data, and it is confirmed that our capacity loss estimation formulas can estimate even complicated test pattern. The estimated capacity retention after 36 seasons (18 years) for a GEO satellite is 77% of the initial capacity. The breakdown is; calendar capacity loss 12%, true cycle capacity loss 11%. From this result, we can judge that the Space 100 Ah Li-ion cells can operate actual GEO satellite too.

Based on these fitting results, it is confirmed that both modified calendar capacity loss formulas and the original true cycle capacity loss formula are in the right. And GYT Space Li-ion cells have sufficient capability to achieve the mission life requirements for several kinds of artificial satellite such as GEOs and LEOs. First flight of GYT space Li-ion cells was implemented in 2003 by SERVIS-1 (experimental LEO satellite). Next, 100 Ah cells were installed in THAICOM-4 (very large commercial GEO satellite) and launched in 2005. The cells are working well now.

We are now planning to perform DPA (destruction physical analysis) of the life test cells and chemical analysis of its electrode materials in near future. We would like to report verification results of our capacity loss mechanism and the formulas by the chemical analysis.

4 Conclusion

Large capacity Li-ion cells with 100 Ah had been evaluated at various conditions for around ten years and high accuracy capacity loss estimation formulas have been derived. The details are shown as follows.

1) Capacity loss of space Li-ion cells can be also explained by the following two mechanisms. One is calendar capacity loss and the other is true cycle capacity loss.

2) SEI growth blocking mechanism for the calendar capacity loss model is proposed. It means that the calendar capacity loss (SEI growth) is blocked by the adjacent SEI layers. The blocking parameter is in proportion to the $2.4$th power of amount of calendar capacity loss.

- Amount of calendar capacity loss $\% = k_f \cdot t^{1/2}$

- $k_f = k_f (1 - \text{amount of calendar capacity loss})^{24}$ The BOL rate constant $k_f$ is function of temperature and SOC.

3) Revalidation of the true cycle capacity loss is performed and it is confirmed that following formula is in the right.

- Amount of true cycle capacity loss $\% = k_c \cdot N^{1/2}$ The rate constant $k_c$ is function of DOD, and we have confirmed that the $k_c$ is not affected by temperature in the range of 15°C to 60°C.

4) GYT Space Li-ion cells have sufficient capability to achieve the mission life requirements for several kinds of artificial satellite such as GEOs and LEOs.

References