

# The Quantitative Evaluation of Anode Thickness Change for Lithium-ion Batteries

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**ABSTRACT** The measurement technique of the electrode thickness to measure the expansion and the contraction of the electrode containing active material as height information during charge and discharge has been established. The behavior that the electrode thickness expands continuously as the number of charge and discharge cycles increases is clarified by a quantitative evaluation of the graphite based electrode and the silicon based electrode thickness and it was confirmed that from the observation of Scanning Electron Microscope (SEM), an accurate electrode thickness measurement after the charge and discharge test has been carried out. It is assumed that the volume expansion continues due to not only the expansion and the contraction behavior of the active material, but also due to the penetration of the electrolyte and the deposition of Solid Electron Interface (SEI) and etc. By observing the electrode change checking the thickness measurement result against the charge and discharge characteristics, the electrode behavior can be clarified and the information for the optimum selection of copper foil can be obtained.

## 1. INTRODUCTION

The application of the lithium-ion secondary battery (LiB) has been expanding as a high-output and a high-capacity battery for the applications of portable devices, electric vehicles and etc. The schematic view of LiB is shown in Figure 1. It is configured by the electrode consisting of an active material and a current collector foil, a separator and an electrolyte. In recent years, the higher capacity of the anode electrode active material has been achieved, but the demand of the current collector thickness reduction for further densification has been increasing. Especially, to reduce the thickness of the negative electrode current collector copper foil, the mechanical property is important to withstand the stress due to the expansion and the contraction of the active material during the charge and the discharge.

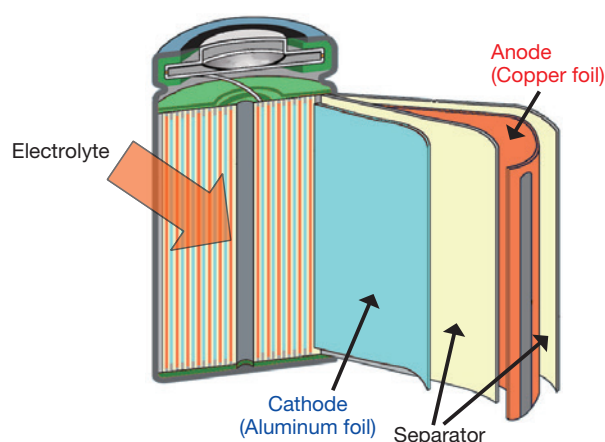


Figure 1 The Schematic View of a Lithium-ion Battery.

For example, the theoretical capacity of the widely used graphite based active material is 372 mAh/g<sup>1</sup>) and the volume expands up to 110% at maximum by the lithium intercalation and de-intercalation between the graphite layers. In contrast, an elemental Silicon (Si) which is a high capacity active material, has the capacity of 4200 mAh/g by alloying reaction with lithium, but the volume expansion is also large up to 400% at maximum<sup>2</sup>). The SiOx based active material developed for the purpose of suppressing the volume expansion of Si has about 1200 mAh/g and it has been already commercialized. The volume expansion is suppressed in comparison to Si based simple substance, but the volume expansion larger than the graphite has been reported<sup>3</sup>). In this manner, in the

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case of anode which uses a high capacity active material, the change during the expansion and the contraction is substantial. Therefore, not only the study to suppress the volume expansion of high capacity active material, but also the quantitative method to evaluate the volume change due to the electrode expansion and the contraction have been sought.

Regarding the lithium-ion battery, there are many battery shapes such as prismatic type, cylindrical type, laminate type and etc. It is considered that in any shapes, the main factors that deform the entire electrode including the anode electrode current collector due to the charge and the discharge are the expansion and the contraction of the active material described before and the SEI from the electrolyte decomposed material. It is known that because of overlapping of these two factors, the expansion, the contraction and the deformation of the coating film occur and because of the anode electrode degradation, the capacity reduction occurs<sup>4)</sup>. To date, various type of measurement methods such as the AC impedance method<sup>5)</sup> and the current pause method<sup>6)</sup> as methods to analyze the degradation due to the volume expansion during the charge and the discharge, in-situ XRD measurement and measurement using emitted light<sup>7)</sup> such as the method to analyze the crystalline form and others have been developed. However, because these methods are indirect to evaluate the expansion and the contraction of the active material which is the direct factor of the degradation and the deformation of current collector and because the volume change cannot be obtained as a number, the quantitative long term measurement technique by the time when electrode degradation occurs in the shape of a simplified battery while maintaining the actual battery structure has been sought.

Some of the documents that have been reported to date as a technique for measuring the electrode thickness are explained. P. Novak<sup>8)</sup> et al. conducted a thickness measurement using a powdered electrode. Under the condition which can eliminate the effect of the counter electrode, the electrode expands by 1 cycle and the thickness increase was observed according to the graphite stage structure at less than 0.3 V vs. Li/Li<sup>+</sup>. Sakai et al.<sup>9)</sup> also shows the measurement result of electrode thickness in the paper about Si based electrode and the thickness measurement for graphite, Si and also SiO<sub>x</sub> based active material during the charge and the discharge was performed, but only the result by 2 cycles is shown in the paper. Although the precise measurement succeeded, the measurement result remains only by 1 cycle and the behavior of the long term thickness change is unknown. Therefore, according to the existing knowledge, the continuous and highly precise measurement of only anode electrode has not been reported and the measurement which can be mentioned about the copper foil deformation behavior has not been reported. Therefore, by establishing the evaluation technique which uses the film thickness measurement equipment during the charge and the

discharge, the trials to clarify the behavior during the discharge quantitatively and to get beneficial information about the deformation of copper foil anode current collector due to the active material expansion and contraction during the charge and the discharge have been made.

In this paper, the result which the expansion and contraction behavior of the graphite based anode active material widely used for existing lithium-ion battery, furthermore, of the next generation Si based active material and also the deformation of current collector due to these expansion and contraction were clarified quantitatively by using film thickness measurement equipment during the charge and the discharge, will be discussed.

## 2. EXPERIMENTAL PROCEDURE

As mentioned in the previous chapters, while maintaining the structure close to the real battery in the form of simplified battery shape, the trial to measure the expansion behavior of the anode electrode as height information has been done for long term quantitative measurement technique when the electrode degradation occurs.

The experiment procedure is described in the followings. The schematic diagram used for this experiment is shown in Figure 2. The commercially available capacitance type thickness measurement equipment was used. To measure a more precise measurement, the condition which is able to carry a highly accurate measurement was established. Inside the battery, using the porous ceramics separator, the distance between the test electrode and the counter electrode is kept constant and it is the condition which no deviation of test electrode height occurs except for the test electrode expansion and contraction due to the charge and the discharge. Furthermore, the precise potential control has been tried by putting the reference electrode in close proximity to the test electrode.

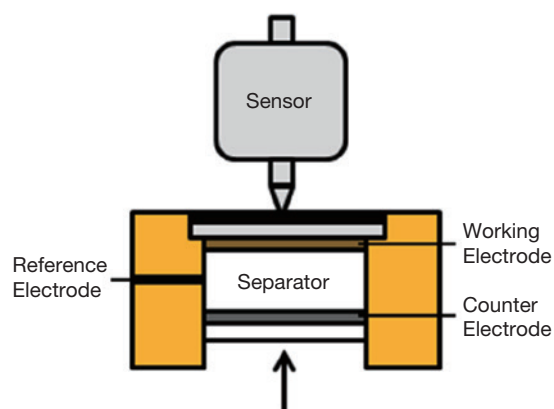


Figure 2 The setup of the electrochemical dilatometer.

By connecting the electrochemical measurement equipment of Solatlon 1280C manufactured by Solatron Company to this equipment and by energizing Constant

Current (CC) or Constant Voltage (CV), the charge and discharge test has been performed. Note that the rate of the charge and the discharge test is kept low constantly and it was confirmed that a uniform charge and discharge is performed on the entire electrode.

### 3. THE EXPERIMENTAL RESULT AND CONSIDERATION

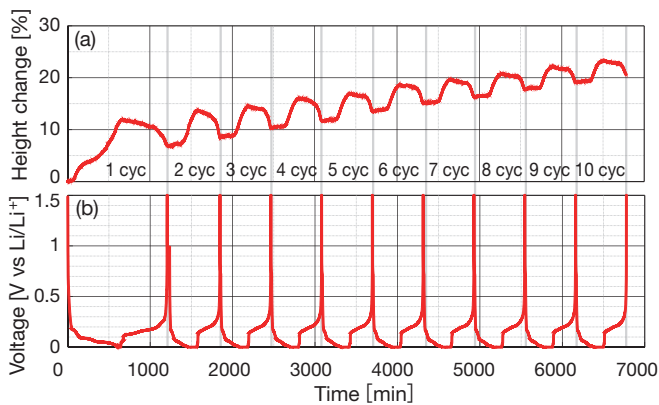
#### 3.1 The Long-term Thickness Measurement Using Graphite Electrode.

The cell configuration is shown in Table 1. At first, an artificial graphite as a standard LiB anode was used for the active material.

**Table 1** The list of charge and discharge condition.

Cell configuration	
Test electrode :	active material composition : artificial graphite/ SBR binder/ CMC=97 : 2 : 1 (weight ratio) one side coating
Counter electrode :	Lithium foil
Reference electrode :	Lithium foil is filled in the configuration of reference electrode.
Electrolyte :	Lithium salt is added to EC/DEC. Temperature: 25°C
Charge and discharge test condition	
Potential range : 0.0 to 1.5 V, cutoff 0.05 C	
1 <sup>st</sup> cycle: 0.1 C, from 2 <sup>nd</sup> cycle: 0.2 C	

Figure 3 shows the relationship between the amount of measured electrode thickness change and the electric potential. In accordance with the switches of the direction from the charge to the discharge, the saw-tooth type expansion and contraction behavior was observed. Because this behavior was observed more than 10 cycles continuously, the result that the continuous expansion and contraction behavior can be measured was obtained.

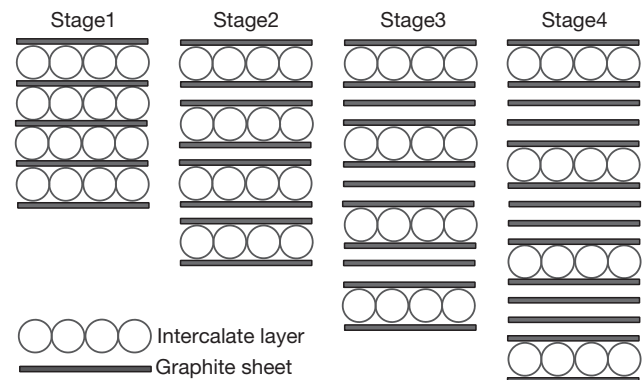


**Figure 3** The measurement result of graphite electrode height using thickness measurement method.  
(a) Height change vs. charge/discharge cycles.  
(b) Potential change vs. time.

Focusing only on the first charge and discharge, the expansion behavior was observed during CC charge and also CV charge. On the other hand, the contraction behavior was observed only during CC charge. At the full charge, the thickness of electrode was increased by 11% compared to the value before charge. In contrast of this, the electrode thickness kept increasing by 6.8% at the end of discharge and it was confirmed that the expanded electrode will not shrink to the thickness before the charge and the discharge. The same behavior was continuously observed after 2nd cycles also and a certain expansion behavior was observed up to 10 cycles.

As a result of the repeated charge and discharge up to 10 cycles, while maintaining a 94% Coulombic efficiency, the electrode thickness is continuously expanding as the number of cycles is increased and the behavior that the volume changes beyond the theoretical value was continuously observed. This result has suggested the possibility that the factor other than the intercalation of lithium-ion to graphite relates to the increase of thickness.

Furthermore, in order to confirm that the thickness change corresponding to the graphite specific potential during the charge and the discharge is measured accurately, the film thickness change was compared to the stage structure theory value which is known in the graphite electrode. The schematic diagram is shown in Figure 4.

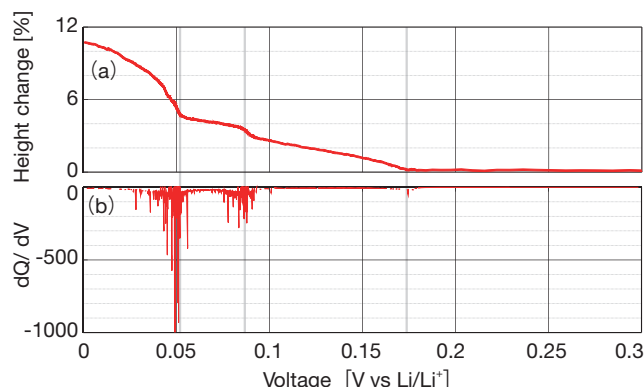


**Figure 4** The schematic diagram of the graphite stage structure<sup>11)</sup>.

The graphite based active material is charged by intercalation of lithium-ion between graphite crystalline layers. At that time, according to the amount of lithium-ion intercalation, it is known that 4 stage structures are taken to change the distance between layers to c axis direction<sup>10)</sup> and the volume expansion due to this is observed. Also, when the stage structure changes, a current response is confirmed<sup>11), 12)</sup> and the current response is obtained by differentiating the quantity of electricity Q (Coulomb) which is charged or discharged by the electrode at the potential V (Voltage vs. Li/Li<sup>+</sup>).

It is assumed that the same stage structure change, the current response and the film thickness change due to these in the film thickness measurement result can be

observed. Therefore, the actually observed current response at 1st charge cycle is shown in Figure 5.



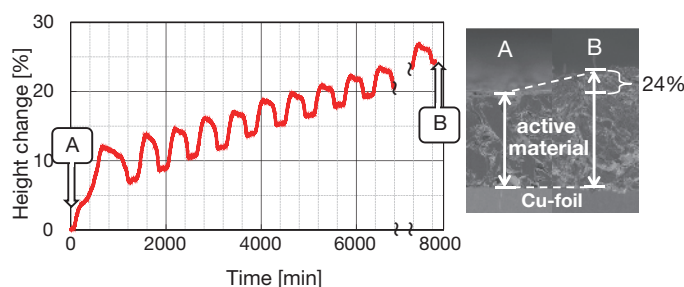
**Figure 5** The measurement result of graphite electrode after 1 cycle.  
(a) Height change (%)  
(b) dQ/dV vs. Voltage (V vs. Li/Li<sup>+</sup>)

As shown in Figure 5, a strong current response was observed at the potential which is estimated when the stage structure changes and the slope of the thickness change behavior have changed. It is considered that the specific stage structure change same as previous report<sup>11)</sup> occurs in the lithium intercalation to graphite. Although the equivalent current response was observed in the discharge side, the response at the time of charge was particularly remarkable. Moreover, comparing the theoretical expansion rate calculated by the electrode thickness change and the stage change potential to the value of paper<sup>12)</sup>, the measured values agree well with the theoretical expansion values at each stage structure.

Because the electrode composition used in this charge and discharge test is almost occupied by the graphite and also the graphite active material<sup>13), 14)</sup> is oriented to C axis direction is used, it is assumed that the measured value which is comparatively agreeable with the theoretical value was obtained. On the other hand, with regards to the film thickness expansion, in addition to the volume change of active material, the void existing in anode itself and the additives such as binder contained in the electrode and etc. contribute largely<sup>15)</sup>. It is considered that this result agrees with the theoretical value because the coating film itself containing the active material is a relatively high density equivalent to the consumer electrode.

To confirm that the actual film thickness agrees with the theoretical value regarding the measurement after finishing the measurement, the SEM pictures of the electrode cross section before and after the charge and the discharge, in conjunction with the measurement result of the electrode thickness after 10 and several cycles were shown in Figure 6, respectively. Point A is the electrode thickness before the charge and point B is the one after finishing the charge. About 24% electrode thickness

expansion in average was observed after charge according to the SEM pictures which measures the active material thickness in the multiple points from the electrode center.



**Figure 6** The graphite electrode measurement result and the SEM image after charge and discharge cycles.  
(A) original  
(B) after the charge and the discharge cycles.

Because the SEM observation agreed with the result at the end of the measurement, it is proven that this electrode thickness measurement is carried out accurately.

By investigating each of the result during the charge and the discharge and after the charge and the discharge, the reasonable result about film thickness measurement was obtained. From this result, it is thought that the measurement technique to measures the long-term (The electrode degradation occurs.) and the qualitative electrode height information as the thickness has been established.

The factor of the continuous electrode thickness increase of graphite based electrode will be discussed. Regarding the film thickness observed this time, 2 factors of the increase other than the lithium intercalation and de-intercalation will be discussed. At first, the anode film thickness increase due to the expansion of the electrode itself will be discussed. The configuration is that even the electrolyte is filled in the cell, the electrode is not immersed completely. Therefore, it is assumed that the penetration of the electrolyte is largely depending on the reaction of the charge and the discharge. Since the charge and discharge efficiency of 2nd cycles are significantly improved against the 1st cycle, it is thought that the expansion due to the penetration of the electrolyte to the active material is involving in the charge and the discharge of 1st cycle.

Next, the deposition of the electrolyte decomposed material from the electrolyte and the formation of SEI will be discussed. In the lithium-ion battery, it is known that the decomposition reaction of the electrolyte occurs. Moreover, as described before, it is known that ion-conducting film derived from the electrolyte decomposition material is formed<sup>1)</sup> and, it is known that the reaction of the lithium-ion intercalation and de-intercalation to the graphite is accelerated because SEI is formed on the surface of the electrode<sup>1)</sup> and the charge and discharge effi-



ciency of anode electrode is improved.

In this measurement result also, it is assumed that the SEI formed material and the reaction deposition material due to the decomposition of the electrolyte are generally observed as the thickness increases. Because the charge and discharge efficiency is improved at 2nd cycles and it was maintained at subsequent cycles, it is assumed that SEI formation is a dominant reaction at 1st cycle. Further, since the tendency for the film thickness expansion to saturate was seen after 2nd cycles, it is assumed that the SEI formation or the electrolyte decomposition occurs after 2nd cycles also. It is thought that these factors contribute in a complex manner so that the battery degradation is accelerated.

### 3.2 The Electrode Thickness Measurement Using Si-based Electrode.

Based on the result of the previous chapters, because the techniques to measure the electrode height information due to the graphite electrode degradation in terms of the thickness quantitatively, the result of the Si based electrode thickness measurement using the current collection copper foil having different mechanical property will be discussed next.

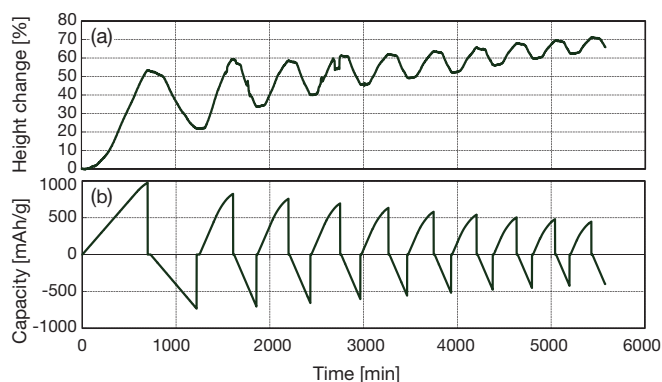
When the charge and discharge test is carried out using different kind of copper foil, it was clarified that the difference occurs in the film retention capability and the difference of volume retention ratio of active material also occur. In the report of Sakai et al.<sup>9)</sup> also, the result that the charge and discharge test using the Si based active material differs according to the copper foil strength is shown and it is reported that in the charge and discharge test using the high strength metal of the SUS foil as an anode current collector, a high charge and discharge efficiency compared to the conventional copper foil is maintained even after the long-term cycles.

It is thought that the difference in the deformation degree due to the current collector foil samples is because the different deformation behavior occurs against the active material expansion by the mechanical characteristic value of the current collector strength and elongation. Especially, in the case where the copper foil adheres to the electrode tightly using organic binder such as polyimide and others, it is considered that the direct stress due to the expansion and contraction is applied to the copper foil and it is plastically deformed. Therefore, aiming to measure, not only the expansion and the contraction of the high capacity material, but also the deformation behavior during the charge and discharge test, the electrode thickness measurement has been performed using the technique established in chapter 3.1.

By mixing the Si based active material and the artificial graphite, the electrode of about 800 mAh/g was designed and the electrode was fabricated by coating it to the one side of the current collector copper foil. To compare the deformation behavior, 2 kinds of copper foils were used. One is a conventional foil with 10  $\mu\text{m}$  thickness and the other is a high strength foil. The condition other than elec-

trode information is equivalent to Table 1 and the charge and discharge test of 10 cycles has been carried out.

At first, the test result of the thickness change behavior using the conventional foil is shown in Figure 7. The thickness change behavior during the charge and the discharge and the discharge capacity are also shown in this figure.



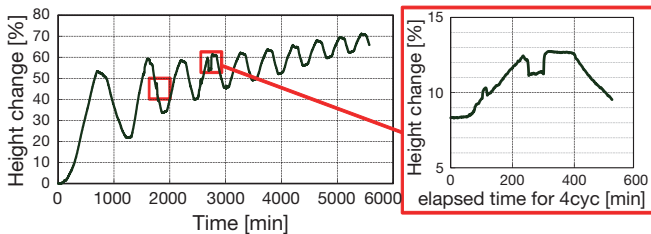
**Figure 7** The result of the electrode height measurement by the thickness measurement technique using a conventional foil. (a) Height change (b) Potential change

The saw-tooth type expansion and contraction behavior due to the charge and the discharge same as the graphite based electrode described in the previous chapter was observed. During CC charge and CV charge the electrode was expanding and during CC discharge, the electrode was contracting. The amount of charge for the first time was 976 mAh/g and the capacity of discharge was 733 mAh/g. The efficiency of the charge and the discharge was 75%. It is assumed that because sub-reaction such as SEI formation occurs, the overcharge occurs. However, the result was that the charge and discharge capacity is reduced continuously after 2nd cycles and the discharge capacity was reduced to about 20% at 10 cycles. With the decrease of the discharge capacity, the phenomenon, where the peak of the saw-tooth type expansion and contraction behavior becomes smaller, was observed. As a cause, it is assumed that because the anode current collector copper foil cannot support the severe expansion and contraction behavior of the Si based active material, the electrode delamination occurs and the discharge capacity is decreased. Also, as described in chapter 3.1, it is clarified that the expansion due to the penetration of the electrolyte, furthermore, the deposition of the electrolyte decomposed material and the SEI formation contribute to the electrode expansion and contraction in conjunction with the expansion and contraction behavior of the active material, respectively, but it is assumed that the copper foil deformation is accelerated because these factors contribute in a complex manner.

From this result, the thickness measurement during

continuous 10 cycles of charge and discharge of the Si based active material was successful for the first time. However, the capacity reduction was severe and the result was difficult to say that the thickness increase behavior due to the sufficient charge and discharge reaction was observed.

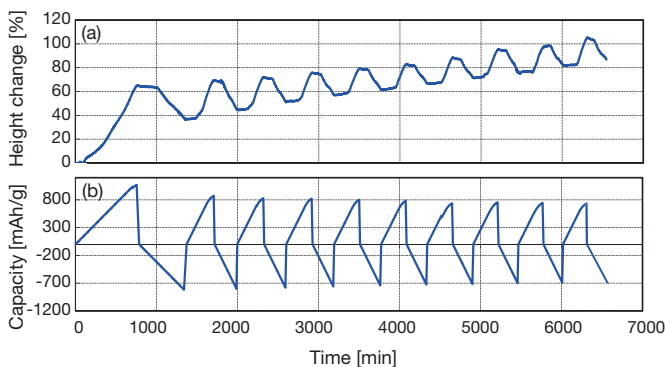
Here, if the thickness change behavior is observed very carefully, the discontinuous height variation different from the expansion due to the charge was observed at 2nd cycles of discharge and at 4th cycles of charge in the charge and discharge test of conventional copper foil. The enlarged figure of its discontinuous variation is shown in Figure 8.



**Figure 8** The enlarged view of the discontinuous height change in Figure 7 (a).

From this figure, because the discontinuous contraction was observed during the charge that the only expansion behavior shall be observed, it was suggested that there was a possibility where the deformation and contraction of the current collector copper foil occurred at this point.

Next, with regards to the test result using the high strength foil, the thickness change behavior and the discharge capacity during the charge and the discharge are shown in Figure 9.



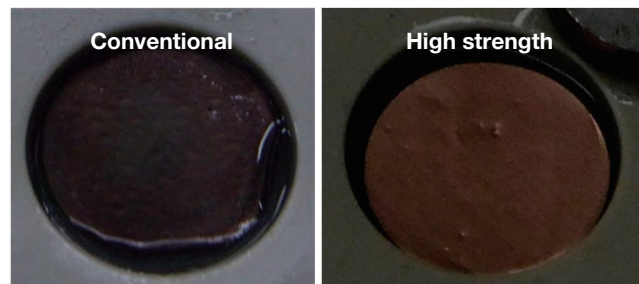
**Figure 9** The measurement result of the Si based electrode height by the thickness measurement technique using the high strength copper foil. (a) Height change (b) Potential change

With regards to the expansion amount of the electrode, the discharge capacity of about 800 mAh/g was achieved at 1st cycle and the charge and discharge efficiency for

the first time was 76.5%. It was confirmed that while maintaining the discharge amount of about 90% against the first discharge amount after 2nd cycles, the charge and discharge continued up to 10 cycles. The fact that the electrode thickness was expanding by 87% at the end of 10 cycles was clarified.

In the case that the high strength foil is used against the conventional foil mentioned before, the discharge amount of about 90% is maintained against the first discharge amount and by using the high strength foil, it was confirmed that there is an effect that the retention of the capacity is improved. It is considered that the delamination and the drop out of the coating film are reduced because the deformation of the current collector is suppressed by using the high strength foil.

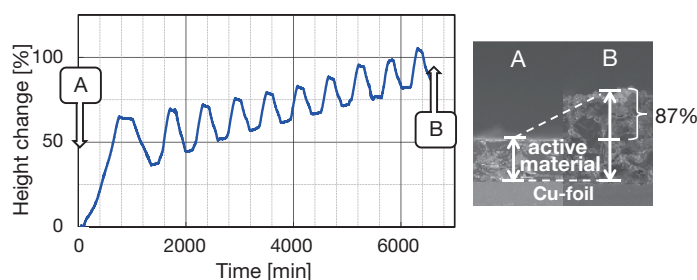
Next, in order to compare the degree of deformation of the current collector copper foil after the charge and discharge test, the picture of the electrode after the charge and discharge test was taken from the side of the current collector copper foil. They look as in photographs shown in Figure 10. In the case of the high strength foil, although there are irregularities on the surface slightly, the phenomenon where the entire current collector is deformed was not observed. Moreover, almost no delamination was observed in the active material coated on the copper foil. In contrast, in the case of the conventional foil, the copper foil warped inside and the electrode deformed largely in the form of a downwardly convex. Also, the coated active material is delaminated largely and very few active materials were adhering to the current collector. From these results of thickness measurement and charge and discharge test, it was confirmed the predicted deformation of copper foil occurs actually.



**Figure 10** The appearance of the electrode after 10 cycles.

After measurement, in order to confirm that the film thickness measurement result agrees with the actual film thickness, the observation of the cross sectional thickness by SEM was performed for the high strength foil in which the active material remained on the surface. The SEM picture before and after the charge and discharge test is shown in Figure 11. From the SEM image, when the electrode in the SEM image is observed, the electrode is expanded by 87% in average and the measured height also agreed so it was confirmed that the electrode

thickness which contains active material was measured accurately.



**Figure 11** The graphite electrode measurement result by the thickness measurement technique and the SEM image after the charge and discharge cycles.

From this result, it was confirmed that with respect to the electrode thickness expansion and the copper foil deformation behavior, those combined results can be measured as the height information.

#### 4. CONCLUSION

- (1) The quantitative and continuous measurement technique of the electrode thickness change has been established.
- (2) The behavior that the graphite based active material and the Si based electrode thickness expands continuously has been clarified.
- (3) It has been clarified that factors other than the expansion and the contraction of the active material will affect largely the actual electrode deformation. As factors, the expansion of the active material layer, the deposition of the electrolyte sub-reaction product and the SEI formation are considered.
- (4) By using the high strength copper foil, the suppression of copper foil deformation and the improvement of the charge and discharge efficiency of the Si based active material have been successful.
- (5) The observation of the deformation behavior of the coating film and the copper foil during the charge and the discharge has been successful.

#### 5. AT THE END

In accordance with the expansion of the lithium-ion battery application such as in mobile equipment and others, it is assumed that the roles and the characteristics of the copper foil to play as a component of the battery will be diversified. In the future, by investigating the comprehensive understanding of the phenomena that occur during the charge and the discharge, we will intensify the knowledge of the anode current collector copper foil through the establishment of the charge and discharge evaluation technique for the next generation battery components.

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