

High Loading Si Anode with 3D Collector and Inorganic Binder

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ABSTRACT

The application of three-dimensional collector and inorganic binder for silicon anodes was investigated with a view to raising the energy density of lithium-ion secondary batteries to a high level. In connection with testing, simulations with compact cells were conducted and confirmed the advantage over conventional electrodes in terms of energy density.

The effectiveness of inorganic binder was confirmed using electrodes (density 0.05 g/cm³) fabricated with a loading mass of about 6.0 mg/cm². It was found that the capacity retention of items without inorganic binder diminished to 25% or less up to the second cycle of the aging process, but the capacity retention of items that included inorganic binder was 78% at 50 cycles. Next, electrode pressing was carried out in order to raise the energy density to a high level. The electrodes obtained in this way (density 0.17 g/cm³ and 0.59 g/cm³) were used to perform the same kind of cycle testing, with the result that while the 0.17 g/cm³ item had the same capacity retention as the unpressed item, the capacity retention of the 0.59 g/cm³ item diminished to 46%. The results from cross-sectional observation of the electrode after testing showed that while the expansion and shrinking of the electrode had been successfully suppressed as anticipated, there were cracks between the interfaces of the composite layer and the collector foil, and the amount of that cracking was confirmed to be greater in the 0.59 g/cm³ item.

1. Introduction

As initiatives involving the government and private sector go forward toward a carbon-free society for the purpose of realizing a sustainable society, Honda is moving ahead with the electrification of power products, motorcycles, and automobiles⁽¹⁾.

Various kinds of secondary batteries can be found on the market, and for automobiles, in particular, lithium-ion secondary batteries (LIB) are widely used for their energy density. Compared to the energy density of gasoline (up to 12000 Wh/kg), however, LIB energy density reaches about 200 Wh/kg at most, so electric automobiles with these cells installed face the issue of a cruising range that is shorter than that of gasoline-powered vehicles^{(2), (3)}. One way to address this issue is to raise the LIB energy density to a

high level. There is energy density that is per unit volume, which is volumetric energy density (Wh/L), and specific energy (Wh/kg), which is energy density per unit weight. When discussing the energy density of the cells that are the subject here, the term used will be volumetric energy density, which is crucial in terms of installation in vehicles.

The volumetric energy density of a battery can be expressed, for example, by the following equation:

$$\text{Volumetric energy density (Wh/L)} = \text{Mean drive voltage (V)} \times \text{Active material capacity density (Ah/g)} \times \text{Electrode density (g/L)}$$

Of these terms, electrode density can be broken down into the amount of active material that exists per unit area, expressed by the loading mass (mg/cm²), and the thickness (μm). In other words, an effective way to raise the energy

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density to a high level is to raise the mean drive voltage, the capacity density, and the electrode density to a high level (realizing a high load of active material and a thinner electrode film).

Up to now, it has been confirmed that applying a three-dimensional mesh structure (hereinafter 3D collector) to the electrode (hereinafter 3D electrode) to increase its loading mass can increase the energy density of the cell by approximately 10%, and that even with the decrease in cycle performance and the increase in internal resistance that can be an issue when increasing the loading mass, this is more advantageous than with conventional electrodes. It has been made clear that this technology is effective for raising the energy density to a high level^{(4), (5)}. The application of high capacity active material to this 3D electrode technology can be expected to further enhance energy density.

An investigation was therefore made into the application to a 3D collector of silicon (Si), which was being studied for a next-generation high capacity anode.

The Si under discussion here for application as active material for the anode has a theoretical capacity density of 4200 mAh/g, and the effective capacity has been confirmed up to about 3600 mAh/g⁽⁶⁾, making this an active material with a capacity approximately 10 times that of the 372 mAh/g of graphite, which is commonly applied to the LIB anode. On the other hand, this same active material expands up to four times in volume during charging and discharging, which means that with each occurrence of another cycle, the expansion and shrinking are repeated so that the composite material that includes the Si active material slips off from the collector foil. Thus the extremely low cycle durability presents issues⁽⁷⁾.

2. Electrode Design Guidelines

Figures 1 and 2 show cross-section scanning electron microscope (SEM) images of the Si electrode with loading mass of 3.0 mg/cm² before and after aging. After aging, it can be confirmed that the expansion of the active material has expanded the electrode thickness by a factor of 1.8, from 25 μ m to 45 μ m. Collapse of the electrode can also be confirmed, and it is apparent that electron transfer has been disrupted. To assure the cycle durability of Si-related electrodes, therefore, it is necessary to reduce the loading mass. Enhancement of each component (active material, binder, conductive agent, and electrolyte) and optimization of electrode specifications and charge-discharge conditions have been recommended as ways to address this issue⁽⁸⁾⁻⁽¹⁰⁾. It is still the case, however, that cycle durability of 100 cycles or more has been confirmed at 3.0 mg/cm² and below, which is one-half or less than the common graphite electrode⁽¹¹⁾⁻⁽¹⁴⁾.

For the present research, therefore, Si was used as the active material and the 3D collector and silicate binder (hereinafter inorganic binder) were combined and an

investigation was made into Si anodes that can show adequate energy density as a cell. An effort was made to mitigate the issue of cycle durability, which arises when loading mass is enhanced, by combining, as shown in Fig. 3, the preservation of micrometer-size structure by means of the lattice structure of the 3D collector with preservation of nanometer-size structure by means of the strong siloxane bond from the inorganic binder, suppressing the splitting apart of the Si particles and of the composite material.

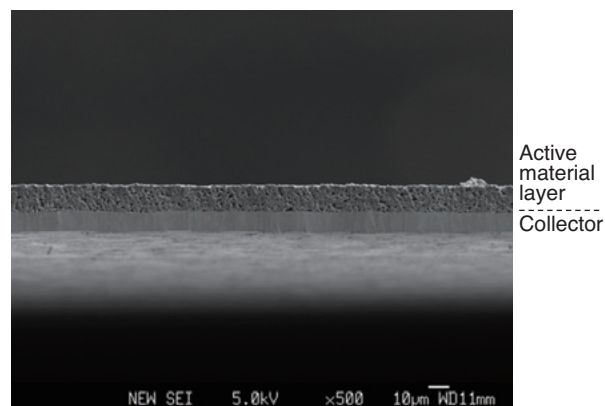


Fig. 1 Cross-section SEM image of Si electrode before aging (magnification: $\times 500$)

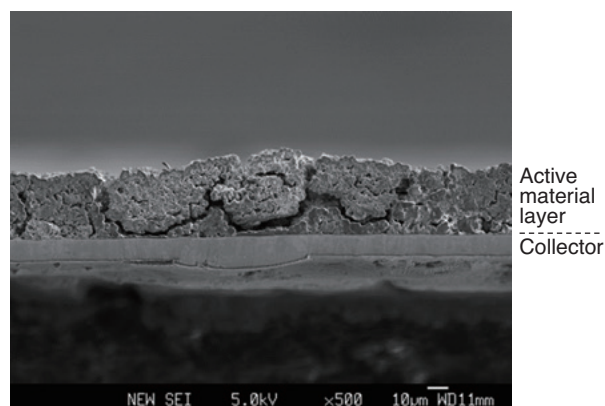


Fig. 2 Cross-section SEM image of Si electrode after aging (magnification: $\times 500$)

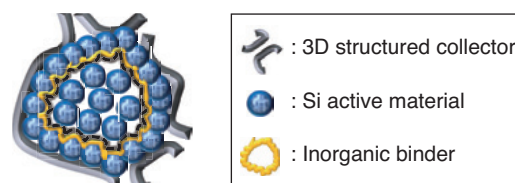


Fig. 3 Image of 3D anode with Si applied

Table 1 Electrode calculation conditions

	Foil coated electrode	3D electrode	3D-Si electrode
Cathode active material	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$		
Cathode active material content	94 wt%		
Cathode collector foil	Al 15 μm	Aluminum Celmet	
Cathode 3D-structured collector porosity	-	97%	
Anode active material	Graphite		Silicon
Anode active material content	96.5 wt%		91%
Anode 3D-structured collector porosity	-	97%	
Element ratio	83 vol%		
Anode collector foil	Cu 8 μm	Nickel Celmet	
Separator	15 μm		
Negative/Positive ratio	1.05		
Cell volume	360 mL		

In addition to the combining of these components, electrode density is also an important parameter. With a low density electrode, for example, it is possible to leave a certain amount of opening in the pole plate so that the strain on the electrode caused by expansion and shrinking can be suppressed. The cycle durability is thereby enhanced, while on the other hand, since there is capacity that volume does not contribute to, the volumetric energy density is decreased. The present investigation, with a view to raising the energy density to a high level, has also been conducted together with investigation of pressing to obtain higher density.

2.1. Calculation of Energy Density

Assuming a cell size of 360 mL and the calculation conditions in Table 1, the volumetric energy density of the cell for varying loading mass was calculated with electrodes using the conventional collector foil (hereinafter foil coated electrode), electrodes using the collector with a three-dimensional structure (hereinafter 3D electrode), and electrodes that use Si-related active material for the collector with a three-dimensional structure (hereinafter 3D-Si electrode). The calculation results are shown in Fig. 4.

The calculation results for the foil coated electrode are shown by a dotted line, those for the 3D electrode by a double line, and those for the 3D-Si electrode by a solid line. The calculation results shown for the 3D-Si electrode were obtained under conditions of electrode density 0.3 and 0.5 g/cm^3 .

With the foil coated electrode, taking into consideration that a loading mass of about 90 mg/cm^2 was the coating limit according to the past Honda evaluation because of diminished binding capacity largely due to uneven distribution of the binder, the volumetric energy density of the cell reaches 581 Wh/L at the highest, while with the 3D electrode, the preservation of macrostructure due to the 3D collector raises the upper limit of the loading mass so that the volumetric energy density of the cell rises as high as 641 Wh/L. This indicates that the increase in volumetric energy density is the result of the reduced amount of

components used, such as the separator and the collector, which do not contribute to capacity, because the high loading of the electrode has reduced the number of layers of electrodes necessary.

In addition to this, the 3D-Si electrode with Si active material applied is found, in a comparison with cathode loading mass at 90 mg/cm^2 , to have 629 Wh/L at low density (0.3 g/cm^3) and 732 Wh/L at high density (0.5 g/cm^3). At the cathode loading mass of 150 mg/cm^2 , the figures are 695 Wh/L at low density (0.3 g/cm^3) and 817 Wh/L at high density (0.5 g/cm^3). According to the above results, cell volumetric energy density can be enhanced by a factor of 1.4 at most relative to the conventional foil coated electrode in calculation.

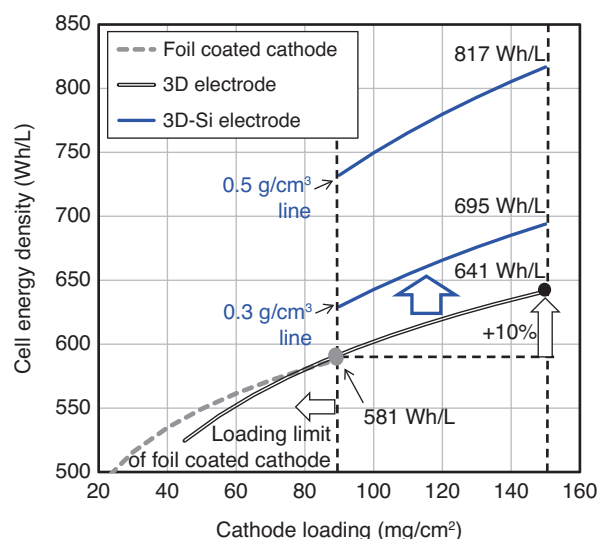


Fig. 4 Relationship between electrode type and cell energy density

3. Testing Method

3.1. Cell Components

3.1.1. Collector with three-dimensional structure

Celmet manufactured by Sumitomo Electric Industries, Ltd., was used for the collector. Aluminum Celmet was used for the cathode and nickel Celmet for the Si-related anode. Ordinarily, copper collector foil is used for a LIB anode, but here the stronger nickel was adopted for the material with the aim of heightening the mechanical strength of the collector as a measure to counter the expansion and shrinking of Si active material.

3.1.2. Cathode

Ternary layered oxide $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) was used for the active material, acetylene black (AB) for the

conductive agent, and polyvinylidene difluoride (PVDF) for the binder, combined with an element ratio of NCM/AB/PVDF = 94/4/2 wt%. After that, the flow shown in Fig. 5 was followed to make the electrode so that after (a) the slurry has been prepared, (b) the electrode coating is applied with a loading mass of 100 mg/cm² on the electrode, after which that electrode is (c) roll pressed to an electrode density of 3.2 g/cm³.

3.1.3. Anode

Table 2 shows the specifications of each electrode. Si powder is used for the active material, AB for the conductive agent, with vapor grown carbon fiber (VGCF), and PVDF as binder with an element ratio of Si/AB/VGCF/PVDF = 91/4.2/0.8/4 wt%. Using this composition, a similar procedure is followed with the cathode to yield an electrode with the loading mass and density shown in Table 2 before coating with the inorganic binder.

The electrode obtained in this way is coated and impregnated with inorganic binder solution (K₂O•3SiO₂) to a loading mass of 1.0 mg/cm² by a spray method with reference to a past document⁽¹⁰⁾. After that, it is heat treated to a temperature of 120°C and the intended electrode is obtained.

This electrode is roll pressed (rolling temperature of 60°C) and electrodes of varying densities, as shown in Table 2, were obtained.

3.1.4. Separator

A microporous polyethylene film of 15 µm thickness was used.

3.1.5. Electrolyte

A mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) was decided on for the solvent, at a ratio of EC/DMC/EMC = 30/40/30 wt%. The electrolyte was made by dissolving the supporting salt lithium hexafluorophosphate (LiPF₆) in a 1.2 mol concentration in the solvent mixture.

3.1.6. Cell exterior body

The CR2032 type coin cell was used for the exterior body here.

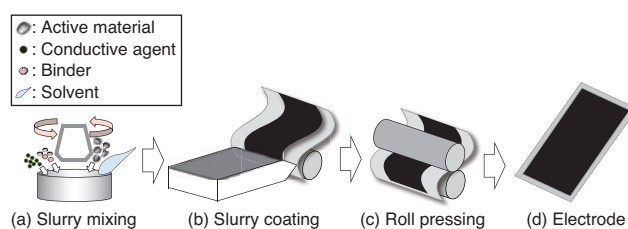


Fig. 5 Lithium-ion battery electrode manufacturing processes

Table 2 Silicon electrode

	Reference	Si-0.05 g/cm ³ (Si-1)	Si-0.17 g/cm ³ (Si-2)	Si-0.59 g/cm ³ (Si-3)
Active material	Silicon			
Active material content	90 wt%			
Electrode loading	6.0 mg/cm ²		5.5 mg/cm ²	5.3 mg/cm ²
Electrode density	0.05 g/cm ³		0.17 g/cm ³	0.59 g/cm ³
Inorganic binder	Not applied	Applied		
Collector	Nickel Celmet			

3.2. Analysis of Electrode

3.2.1. Scanning electron microscope

Cross sections prepared using a cross-section polisher were observed using an ULTRA 55 SEM from Carl Zeiss AG for the purpose of confirming the state of collector contact with active material in the electrode.

3.2.2. Energy dispersive X-ray spectrometry analysis

Energy dispersive X-ray spectroscopy (EDX) with equipment from JEOL Ltd. was used to perform element mapping (C, F, K, Si, and Ni) of the above cross-sections for the purpose of confirming the dispersibility of the active material, conductive agent, and binder in the electrode. Of the elements, C indicates the presence of conductive agent and binder, F the presence of binder, K the presence of inorganic binder, Si the presence of active material, and Ni the presence of collector, respectively.

3.3. Cell Evaluation Method

The cells were placed in a thermostatic chamber at 45°C and each subjected to charge-discharge cycle testing at a constant current of 0.1 C in the range from 4.2 to 2.5 V. Measurements were made with a rest time of one hour. For this testing, five charge-discharge cycles were implemented at a constant current of 0.1 C as aging treatment, after which a total of 50 cycles were implemented.

4. Results and Discussion

Figures 6 to 8 show the cross-section SEM results for each three-dimensional electrode with Si applied at Si-0.05 g/cm³, Si-0.17 g/cm³, and Si-0.59 g/cm³ (hereinafter Si-1, Si-2, and Si-3) before cycle testing. Figures 9 to 11 show the respective results for element mapping using EDX.

Si-1, which is a post-coating electrode, has a film thickness and opening structure (outlined in red in the figures) as the pre-coating collector. In contrast to Si-1, however, Si-2 and Si-3 are samples that have been put through pressing to adjust the density to 0.17 g/cm³ and 0.59 g/cm³, respectively, and it was confirmed that the increase in their density is accompanied by a decrease in large openings that are due to the structure itself, whereas in Si-3 there are none as far as can be determined from cross-section images.

The EDX results for each electrode also confirm that conductive agent (C image) and binder (F image: PVDF; K image: inorganic binder) are present in every sample in

the active material shown in the Si image. In Si-3, however, there is contrast in the K image inside and outside the electrode, suggesting that the amount of inorganic binder inside the electrode is not adequate.

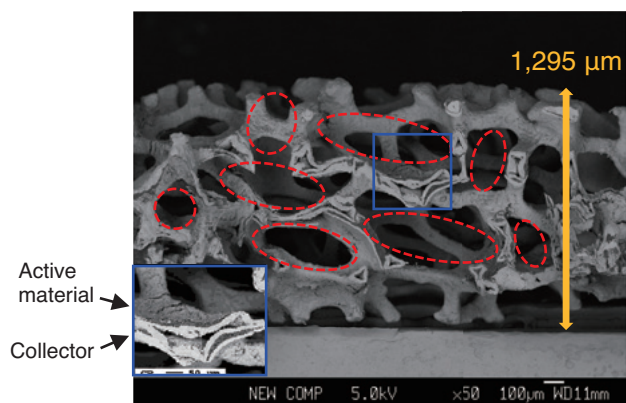


Fig. 6 Cross-section SEM image of Si-1 before test (magnification: $\times 50$)

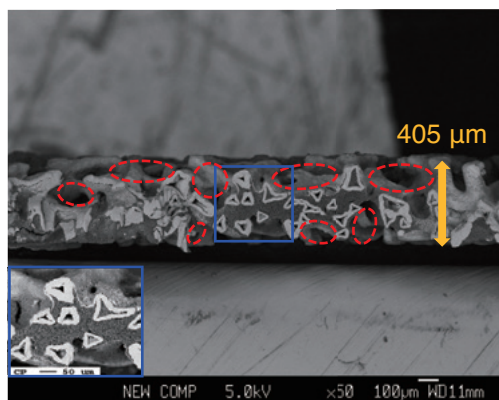


Fig. 7 Cross-section SEM image of Si-2 before test (magnification: $\times 50$)

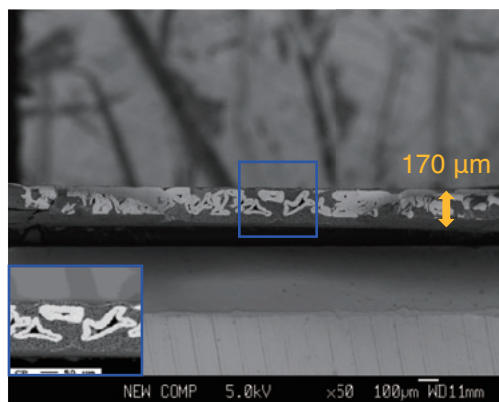


Fig. 8 Cross-section SEM image of Si-3 before test (magnification: $\times 50$)

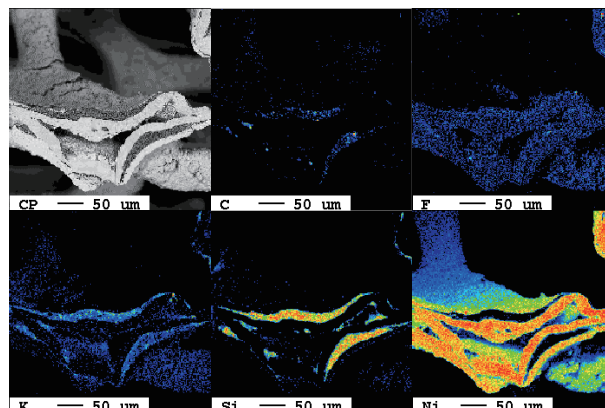


Fig. 9 Cross-section EDX images of Si-1

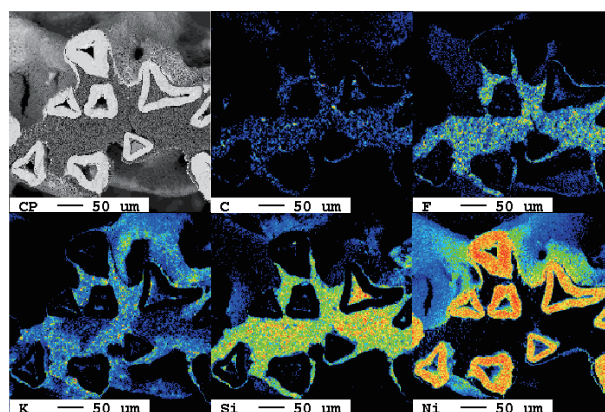


Fig. 10 Cross-section EDX images of Si-2

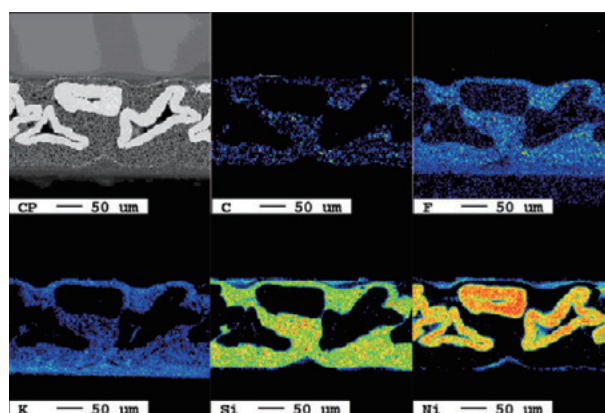


Fig. 11 Cross-section EDX images of Si-3

Figure 12 shows changes in charging capacity with the reference item and with Si-1 during aging (five cycles). In the reference item, capacity retention relative to initial capacity had decreased as far as 25% at the second aging cycle. In Si-1, however, it was at 78%. It was confirmed from these results that the preservation of micro structure by the inorganic binder was effective even in the series to which the three-dimensional collector was applied.

Figure 13 shows the discharge capacity of each electrode with different density (Si-1, Si-2, and Si-3) before and after cycle testing. Figure 14 shows the relationship

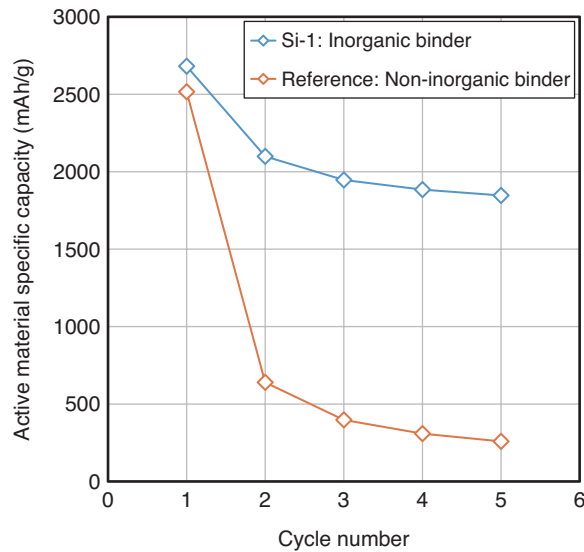


Fig. 12 Charge capacity in aging process of reference item and Si-1

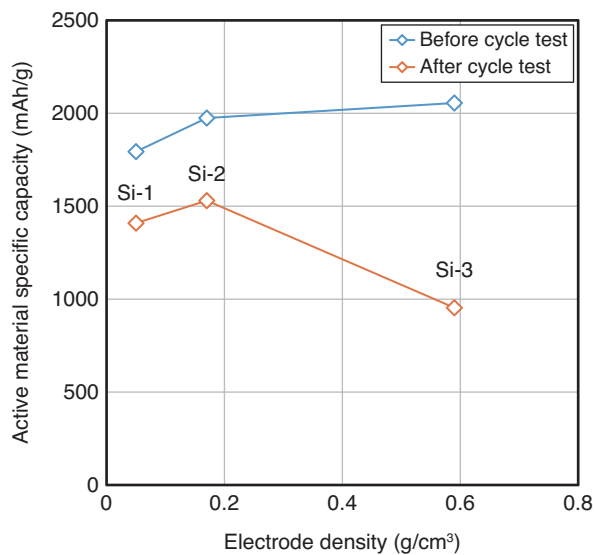


Fig. 13 Discharge capacity of each electrode before and after cycle test

between cycle number and capacity retention. The initial discharge capacities for Si-1, Si-2, and Si-3, in that order, were 1794, 1975, and 2055 mAh/g. This enhancement of capacity is thought to be due to the higher density, which enhanced the contact characteristics of the conductive agent, the active material, and the collector. On the other hand, the discharge capacities after 50 cycles had passed were, in the above order, 1409, 1530, and 954 mAh/g. Looking also in terms of capacity retention, these were 78%, 77%, and 46%, respectively. In terms of cycle durability, this suggested that lower density items had an advantage. The main factors in this are thought to be the openings in the electrode, which functioned as a layer to buffer the expansion and shrinking of the Si active material, and the dispersibility of the inorganic binder. The above results indicate that with the specifications applied here, 78% capacity retention can be achieved at the 50 cycle point even with high loading. They also indicate that discharge capacity and capacity retention are dependent on electrode density.

Figures 15 to 17 show low-magnification (50 power magnification) cross-section SEM images of each electrode removed after cycle testing. Figures 18 to 20 show their high-magnification (2000 power magnification) cross-section SEM images.

From the low-magnification SEM images, the film thicknesses of electrodes Si-1, Si-2, and Si-3, in that order, were found to be 1057, 487, and 200 μm . The cross-section SEM images in Figs. 6 to 8 indicated film thicknesses before cycle testing on 1295, 405, and 170 μm , respectively. In this light, the highest rate of electrode expansion before and after cycle testing is in Si-2, by a factor of about 1.2 at most. From the electrode configurations investigated here, a reduction to about 25% by comparison with the coated

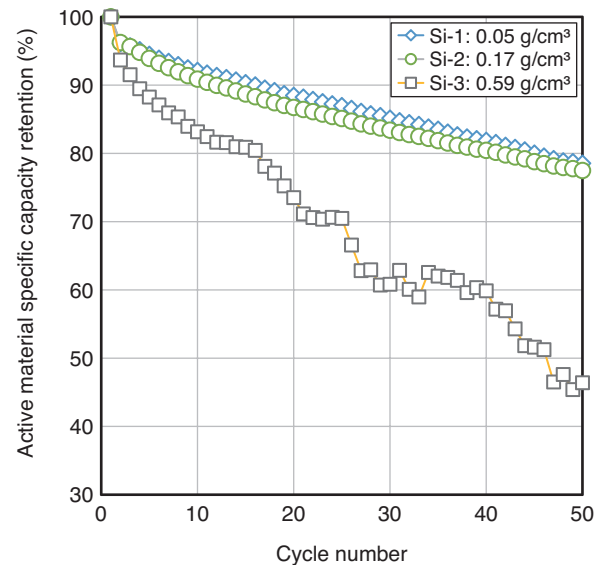


Fig. 14 Capacity retention of Si-1, Si-2, and Si-3

electrodes was confirmed. This is thought to result from the suppression of splitting apart and slipping off in the active material. This suppression occurs because of micro

structure preservation by inorganic binder in the active material and also because this is combined with application of the 3D collector, which can be expected to provide three-

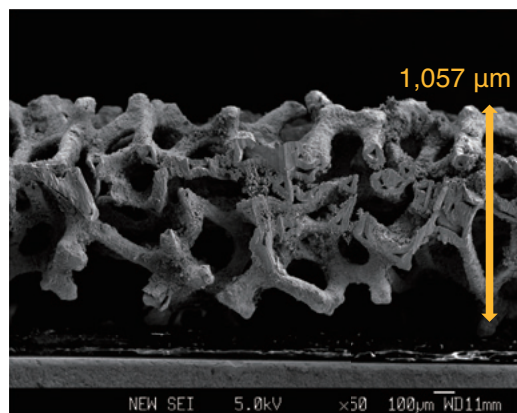


Fig. 15 Cross-section SEM image of Si-1 after test (magnification: $\times 50$)

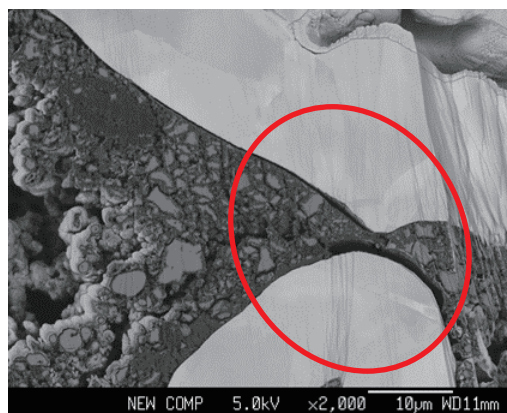


Fig. 18 Cross-section SEM image of Si-1 after test (magnification: $\times 2000$)

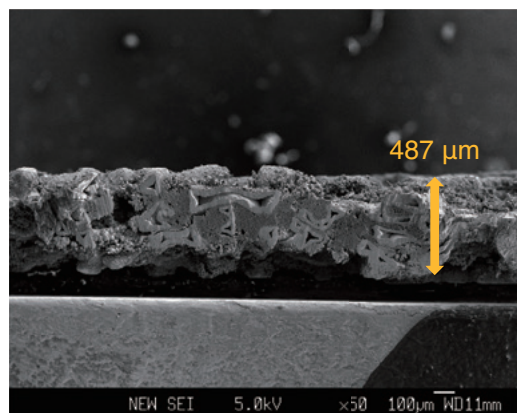


Fig. 16 Cross-section SEM image of Si-2 after test (magnification: $\times 50$)

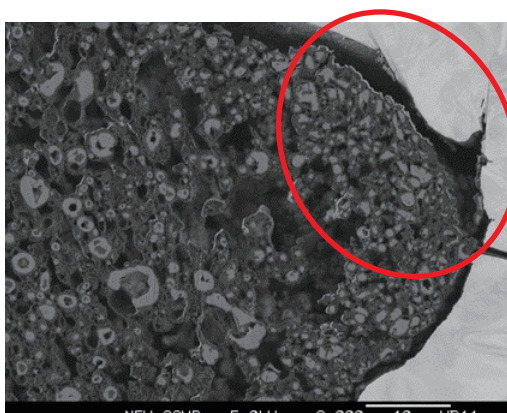


Fig. 19 Cross-section SEM image of Si-2 after test (magnification: $\times 2000$)

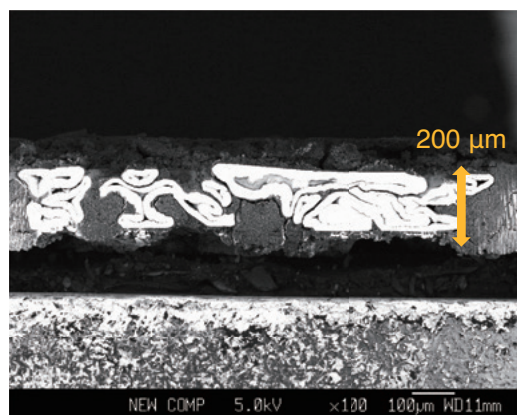


Fig. 17 Cross-section SEM image of Si-3 after test (magnification: $\times 50$)

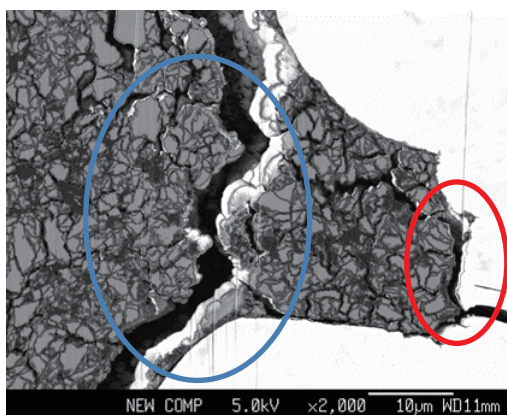


Fig. 20 Cross-section SEM image of Si-3 after test (magnification: $\times 2000$)

dimensional structure preservation from the expansion and shrinking of the active material. It is also the case that in Si-1, the electrode film rather shrinks in thickness, but since these electrodes are unpressed items, this is thought to occur because of the influence of shrinkage under the constraining load of the coin cell. According to the above results, these specifications are confirmed to be an effective means for achieving a balance between high loading with Si-related anodes and high durability.

On the other hand, high-magnification cross-section SEM images confirmed that cracks occur, in the cases of Si-1 and Si-2, between the collector foil and the active material composite layer (outlined in red in Figs. 18 and 19), and in the case of Si-3, between the collector foil and the active material composite layer (outlined in red in Fig. 20) as well as in the active material composite layer (outlined in blue in Fig. 20). It is thought that the cracks in the composite layer lead to isolation of the active material and an increase in resistance that accompanies the interruption of conductive paths, such that capacity retention decreases as a result. It is also thought that, in the cases of Si-1 and Si-2, openings exist in the electrode that are due to the structure itself, and these function as a layer to buffer the expansion and shrinking of the composite layer. In the case of Si-3, however, capacity retention is thought to have been lower because almost no openings exist, and as a result there is a large dynamic load on the interface of the collector foil and the active material composite layer so that cracks also occur in the interface between the collector foil and active material as well as in the composite layer.

The above results confirmed that with the specifications applied here, collapse of the electrode early in the cycles was suppressed even with high loading, but minute cracks in the vicinity of the collector interface caused the interruption of conductive paths, which led to diminished capacity retention. Going forward, it is thought that, in order to suppress the minute cracking, optimization of materials and electrode specifications as well as of charge-discharge conditions will be necessary for the purpose of further enhancing cycle durability with a view to practical application.

5. Conclusion

An investigation was made into the application of a three-dimensional collector and inorganic binder to high loading Si anodes with a view to raising the energy density of lithium-ion secondary batteries to a high level.

- (1) The application of a three-dimensional collector as well as of inorganic binder with a loading mass of about 6.0 mg/cm² yielded a capacity retention of 78% at the 50-cycle point.
- (2) The results from disassembly analysis of the electrode show, on the one hand, that every electrode expands by a factor of no more than about 1.2 at most, and the specifications presented here contributed to suppression

of the expansion and shrinking that is an issue for Si-related anodes. On the other hand, however, the presence of cracks was confirmed between the collector foil and the composite layers as well as in the composite layers.

Going forward, further optimization of specifications of components and electrodes will be pursued with a view to suppression of the cracking that is considered a degradation factor.

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