

Reduction of Internal Resistance in High Capacity Lithium-ion Batteries with 3D Lattice-structured Electrode

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ABSTRACT

After applying a 3D metal lattice structure to the current collectors, enhancements to the cathode were examined in small cells, and an increase in volumetric energy density was demonstrated in laminated cells, with the goal of increasing the energy density of lithium-ion batteries.

Countermeasures were implemented to address two issues with the cathodes of small cells. The efficacy of these measures was confirmed, and the causal factors were cataloged. The first issue is enhancing the contact between the collectors and the active materials. This was addressed by coating the surface of the collectors with conductive carbon. The second issue is enhancing the creation of electron-conductive paths. This was addressed by applying a fine particle conductive agent in the form of a liquid dispersant. The results confirmed that each of these countermeasures had the effect of suppressing resistance and enhancing durability. Moreover, to ascertain the primary cause of these effects, the conductivity of the active material was evaluated using scanning probe microscopy (SPM). The results showed that it is because the countermeasures are suppressing the interruption of electron-conductive paths.

Increasing the thickness of the electrodes in laminated cells reduced the number of electrode layers, and resulted in a 9.8% increase in energy density of cell elements for a cell using 3D lattice-structured electrodes (674 Wh/L), compared with a cell using foil-coated electrodes (614 Wh/L).

1. Introduction

Enhancing fuel economy through electrification of automobiles, and achieving full widespread adoption of electric vehicles, are key measures toward the realization of a low-carbon society^{(1), (2)}. In order to meet the increase in demand, increasing the volumetric energy density of lithium-ion batteries has become a crucial issue^{(3), (4)}.

Volumetric energy density is calculated as the product of battery capacity and average voltage divided by volume. Battery capacity is determined by the capacity per unit volume of active material in the electrodes, and the amount of active material filling the cell. The number of electrode layers can be reduced by increasing the thickness of the electrodes. As a result, the separator and collector amounts used can be reduced. This increases the ratio of active material in the cell, and makes it possible to increase the energy density of the battery.

A study was made of applying a 3D lattice structure to the collectors (3D collectors) of lithium-ion batteries, as a technology to increase the thickness of electrodes by increasing the amount of active material filling the cell. A 3D collector has a porosity of 90% or higher, making it possible to increase the loading by filling the voids with active material^{(5), (6)}. As a result, compared with the usual foil-coated electrodes, electrodes with 3D collectors (3D electrodes) make it possible to reduce the number of electrode layers within a cell. Because the number of electrode layers is reduced, the number of separator layers and the amount of collector used decreases as well. This serves to increase the ratio of active material inside the cell. Consequently, it becomes possible to increase the energy density of a battery through the application of 3D electrodes.

In the previous paper, a prototype cathode using a 3D collector (3D cathode) was fabricated, and the characteristics of the electrode were assessed. This revealed

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its effectiveness at suppressing internal cell resistance and increasing durability compared with foil-coated cathodes⁽⁷⁾. In doing so, two issues were identified with regard to suppressing internal resistance. The first is that enhancement of the collector surface is needed in order to increase contact between the active materials and the collectors. The second is that enhancement of the dispersion characteristics of the conductive agent is needed to increase formation of electron conductive paths between the active materials⁽⁷⁾.

Therefore, remedial measures were considered for each of the two aforementioned issues, with the aim of suppressing the internal resistance of the 3D electrodes. In order to increase contact between the active material and the collector, a 3D electrode with a coating of conductive carbon particles on the collector surface was explored. In order to increase the formation of electron conductive paths between the active materials, the application of a fine particle conductive agent in the form of a liquid dispersant was explored.

Furthermore, a laminated cell was fabricated with 3D collectors applied to both poles, and the increase in energy density was examined.

2. Examination of Cell Structure

2.1. Examination of Contact between Cathode Active Material and Collector

Figure 1 shows the results for a scanning electron microscope (SEM) observation of a cross section of a 3D electrode. As the broken line in the figure shows, a portion of the active material near the collector aluminum of the 3D electrode contains gaps where it is not in direct contact with the collector. Electrons are supplied directly to the active material that is in contact with the aluminum, but the supply of electrons at locations that are not in contact occurs through the mediation of other active materials or conductive agents. This causes the resistance to increase.

A method for coating the surface of aluminum with conducting carbon particles has been proposed as a means of increasing contact between the active materials and the

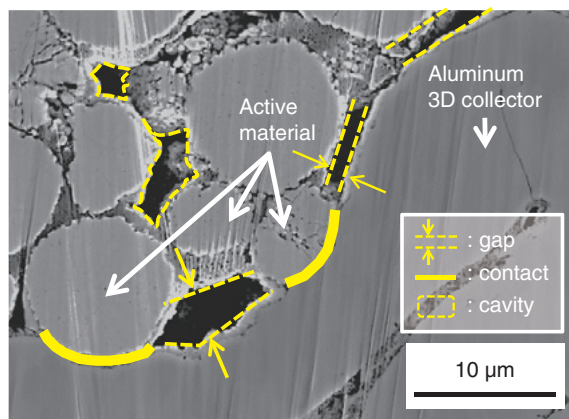


Fig. 1 Cross-section SEM image of 3D cathode

collectors in typical foil-coated electrodes⁽⁸⁾⁻⁽¹⁰⁾. Enhancing the contact between the active materials and the collectors by forming a carbon coat layer decreases interface resistance between the aluminum surface and active materials, while also making it possible to reduce variability in resistance⁽¹⁰⁾. Coating the surface of the aluminum framework of the 3D collector with carbon is expected to eliminate these gaps and effectively increase contact between the active material and the collector. On the other hand, due to the plasticity of the graphite, which is the active material in the anode, there is no issue with contact between it and the collector.

2.2. Examining Electronic Conductivity between Active Materials

In the electrodes of typical lithium-ion batteries, increasing the dispersive properties of the conductive agent is known to help the conductive agent to fill pores evenly, thereby enhancing electronic conductivity between active materials⁽¹¹⁾. Figure 2 shows the measurement results for pore size distribution in a foil-coated cathode and 3D cathode. It can be seen that the pore sizes are smaller in the 3D cathode than in the foil-coated cathode. Moreover, as shown by the broken outlines in Fig. 1, it is clear that there are cavities between the active materials where the conductive agent has not penetrated between the particles of each active material. As the dispersion of the conductive agent decreases, the electronic conductivity within the electrode decreases, causing the electrical resistance to increase⁽¹¹⁾. To counteract this, it is possible to suppress agglutination and enhance the fill of conductive agent into pores, by applying a conductive agent that has been dispersed within a solvent beforehand, instead of a conventional conductive agent powder. Moreover, decreasing the size of the particles

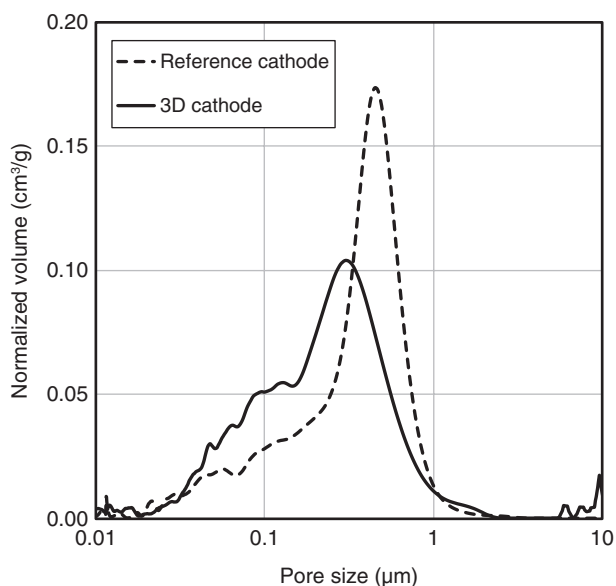


Fig. 2 Cathode pore distribution

in the conductive agent can be expected to have the effect of increasing penetration between the particles of active material, and enhancing electronic conductivity between the particles of active material.

2.3. Examining Energy Density

The previous paper presented the results of calculation of the increase in energy density in a cell to which 3D electrodes have been applied. For the cell size used in vehicles (360-mL volume), the relationship between electrode loading and collector porosity, which makes it possible to surpass the energy density achieved using foil-coated electrodes, was resolved. The results were: 97% or higher porosity at a loading of 90 mg/cm², 93% or higher at 120 mg/cm², and 89% or higher at 150 mg/cm²⁽⁷⁾. For 3D electrodes, the decrease in components due to the decrease in number of layers, which is made possible by thicker electrodes, increased energy density regardless of cell size.

As Fig. 3 shows, lithium-ion battery cells can be divided into a layered element composed of electrodes and separators, and an exterior body of tabs, laminate film, etc. If the active materials are fixed in place, the capacity of the battery is determined by the capacity of the element, regardless of the shape of the cell. Therefore, the effects on energy density of enhancements to the electrodes can be assessed by measuring the capacity per element and comparing the energy densities.

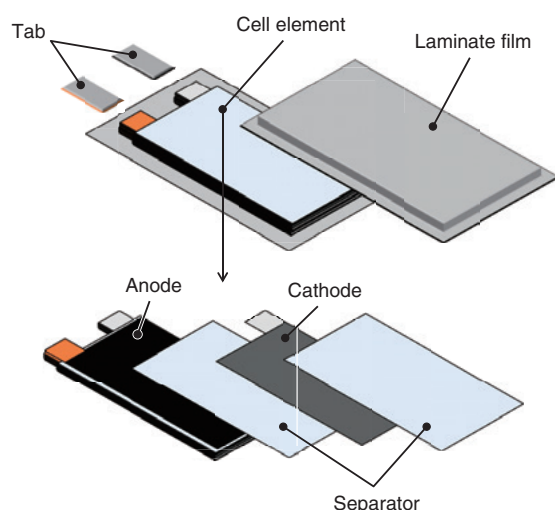


Fig. 3 Internal structure of lithium-ion battery

3. Testing Method

3.1. Cell Components

3.1.1. 3D collector

For the collector, Celmet manufactured by Sumitomo Electric Industries, Ltd. was used^{(5), (6)}. In the interest of battery potential, and because of their stability when used as collectors, aluminum Celmet was used for the cathode,

Table 1 Physical properties of Celmet

	Aluminum Celmet	Copper Celmet
Porosity (%)	97	97
Average pore size (μm)	550	550
Specific surface area (m ² /m ³)	5500	5500
Thickness (μm)	1000	1000
Area density (g/m ²)	100	200

and copper Celmet was used for the anode. Typical physical properties are listed in Table 1.

A 3D collector was fabricated and its aluminum surface coated with a carbon coat layer as shown in Fig. 4. First, a 10-wt% carbon black solution was prepared using N-Methyl-2-pyrrolidone as the solvent. The aluminum 3D collector was then immersed in this solution. Next, a blade was used to remove excess carbon black, and then air was blown over the collector. Finally, this was placed in a vacuum dryer at 120°C to create a carbon-coated 3D collector.

Three types of collectors were created, with carbon coatings of 0.1 mg/cm², 0.5 mg/cm², and 1.0 mg/cm². However, at 0.1 mg/cm² the aluminum surface was not coated evenly, and at 1.0 mg/cm² the voids in the 3D lattice were clogged with carbon. Owing to this, only the evenly coated 0.5 mg/cm² type was made into electrodes.

3.1.2. Cathode

The ternary layered oxide LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) was used as the active material, acetylene black (AB) was used as the conductive agent, and polyvinylidene difluoride (PVDF) was used as the binder. These were combined with a composition ratio of NCM/AB/PVDF = 94/4/2 wt%. The aluminum 3D collector was filled with composite slurry to have a loading of 90 mg/cm². The cathode was then pressed in a roller press at 120°C so that the electrode density would be 3.2 g/cm³, and fabrication of the electrode was completed. The carbon-coated 3D collector was applied, and a cathode was fabricated in the same way as outlined above. In addition to AB, CSB-2 was used. This is a fine particle conductive agent dispersed in a N-Methyl-2-pyrrolidone solvent, from the Conductive Slurry for Battery (CSB) Series manufactured by Mikuni-Color Ltd.; and a cathode was fabricated in the same way as outlined above. Typical physical properties for each conductive agent are listed in Table 2. Because CSB-2 has a smaller particle size

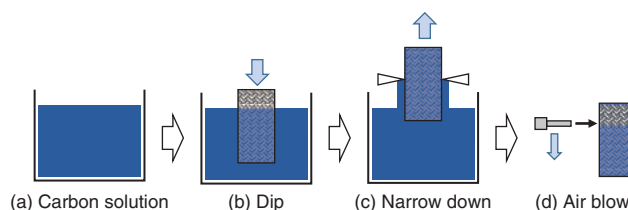


Fig. 4 Schematic view of electrode carbon coating process

Table 2 Physical properties of conductive agent

	AB	CSB-2
Particle size (nm)	48	23
SSA (m ² /g)	41	133
DBP absorption (ml/100g)	114	220
State	Powder	Dispersion

than AB, the specific surface area increases. Accordingly, the amount of di-n-butyl phthalate (DBP) supplied (which indicates solution permeability) is increased. This can also be expected to have the effect of enhancing the permeability of the electrolyte. The foil-coated cathode was fabricated to have an electrode density of 3.2 g/cm³ by coating both sides of a 15- μ m sheet of aluminum foil, so that the loading on each side would be 90 mg/cm² and 45 mg/cm², respectively.

3.1.3. Anode

For the active material, natural graphite (Gr) was used; for the conductive agent, AB; for the binder, styrene butadiene rubber (SBR); and for the thickening agent carboxymethylcellulose (CMC). These were combined in a composition ratio of Gr/AB/SBR/CMC = 96.5/1/1.5/1 wt%. This composite slurry was used to fill both sides of a copper 3D collector so that the loading on each side would be 45 mg/cm² and 22.5 mg/cm², respectively. The anode was then pressed in a roller press at room temperature so that the electrode density would be 1.5 g/cm³, and fabrication of the electrode was completed.

Meanwhile, the foil-coated collector anode was fabricated by coating both sides of a 10- μ m sheet of copper foil, so that the loading on each side would be 45 mg/cm² and 22.5 mg/cm², respectively. The anode was then pressed in a roller press at room temperature so that the electrode density would be 1.5 g/cm³, and fabrication of the electrode was completed.

3.1.4. Separator

A microporous polyethylene film 15 μ m thick was used.

3.1.5. Electrolyte

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

3.1.6. Cell exterior body

A laminate film with a thickness of 150 μ m was used.

3.2. Cell Manufacturing Method

3.2.1. Small cell evaluation

A small cell evaluation was conducted for the purpose of evaluating the internal resistance and cycling properties

of the 3D cathode. Small cells can be easily prototyped with high reproducibility. Also, it is possible to perform a relative comparison of internal resistance and initial durability, making them useful when considering electrode design. Four types of cathodes were subject to investigation: a cathode with a composite-coated collector foil (foil-coated cathode), a cathode with a 3D collector filled with composite (3D cathode (standard)), a 3D cathode coated in a carbon layer (3D cathode (C coating)), and a 3D cathode to which a CSB-2 conductive agent has been applied (3D cathode (CSB-2)). The cathodes were punched out to be 30 mm $\times$ 40 mm in size, the anodes 34 mm $\times$ 44 mm in size, and the separators 40 mm $\times$ 50 mm in size. As Fig. 5 shows, the cell elements were fabricated by placing electrodes and separators in layers. The laminate film was punched out to be 88 mm $\times$ 220 mm in size, then folded in half. The elements were placed inside it and electrolyte injected, then defoamed and sealed to fabricate the laminate cells. Three of each type of cell were prepared and the average values they yielded were used as the evaluation results. Each configuration is also shown in Table 3.

3.2.2. Laminated cell evaluation

A laminated cell evaluation was conducted for the purpose of empirically studying the energy density when 3D electrodes are used for the cathode and anode, and to clarify the resistance in such a cell. With laminated cells, the energy density for the cell can be confirmed, and the resistance value for the cell including tabs and components can be made clear. The cathode was punched out to be 71 mm $\times$ 81 mm in size, the anode 75 mm $\times$ 85 mm in size, and the separator 80 mm $\times$ 90 mm in size. As Fig. 6 shows, the reference electrode cell and 3D electrode cell were each fabricated by placing electrodes and separators in layers. The laminate film was punched out to be 125 mm $\times$ 135 mm

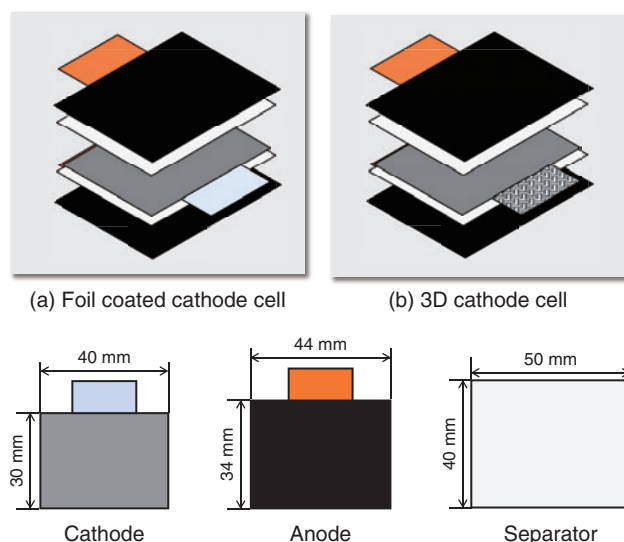


Fig. 5 Small cell element

Table 3 Small cell components

	Foil coated cathode cell	3D cathode cell
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 loading	45 mg/cm ²	90 mg/cm ²
Cathode density	3.2 g/cm ³	
Cathode collector	Aluminum foil	Aluminum Celmet
Anode active material	Graphite	
Anode active material content	96.5 wt%	
Anode loading	22.5 mg/cm ²	
Anode density	1.5 g/cm ³	
Anode collector	Copper foil	
Electrolyte	1.2 mol LiPF ₆ EC/DMC/EMC = 30/40/30 wt%	
Separator	15 μm	
Negative/Positive ratio	1.2	

Table 4 Multilayer cell components

	Reference cell	3D cell
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 loading	45 mg/cm ²	90 mg/cm ²
Cathode density	3.2 g/cm ³	3.2 g/cm ³
Cathode collector	Aluminum foil	Aluminum Celmet (C coating)
Anode active material	Graphite	
Anode active material content	96.5 wt%	
Anode loading	22.5 mg/cm ²	45 mg/cm ² , 22.5 mg/cm ²
Anode density	1.5 g/cm ³	1.5 g/cm ³
Anode collector	Copper foil	Copper Celmet
Number of electrodes	9	5
Electrolyte	1.2 mol LiPF ₆ EC/DMC/EMC = 30/40/30 wt%	
Separator	15 μm	
Negative/Positive ratio	1.2	

in size, placed on the top and bottom of the element, and sealed on three sides. Electrolyte was then injected, and then defoamed and sealed to fabricate the laminate cells. Three of each type of cell were prepared and the average values they yielded were used as the evaluation results. The cell configuration is also shown in Table 4.

3.3. Cell Evaluation Method

3.3.1. Rated discharge test

A rated discharge test was conducted to confirm cell capacity. As an aging treatment, the cells were placed in a thermostatic chamber at 25°C and charged at 0.1 C under constant current (CC), with the upper voltage limit at 4.2 V. After charging under constant current-constant voltage

(CCCV) for a constant voltage (CV) time of one hour, the cells were rested for one hour, then discharged at CC at 0.2 C, with the lower voltage limit at 2.5 V. This constituted one cycle and a total of five cycles were carried out. Cell capacity was defined as the capacity after CC charging at 0.3 C with the upper voltage limit at 4.2 V, charging for a CV time of one hour, then resting for one hour, after which the cell was discharged at CC at 0.3 C, with the lower voltage limit at 2.5 V. For the definition of the C-rate, the current value for full discharge in one hour is taken to be 1 C, where C is the cell capacity divided by the full discharge time. In other words, for a cell with constant capacity, 0.5 C is the current value for full discharge in two hours, and 2 C is the current value for full discharge in 0.5 hour.

3.3.2. 10-second direct current resistance (10-sec DCR)

A 10-sec DCR test was conducted to evaluate the internal resistance of the cell. The state of charge (SOC) of the cell was adjusted to 50%. Next, the cell was discharged for 10 seconds at each set current value and the voltage was measured at 0.1 second, 1 second, and 10 seconds of discharge time. The set current values were 0.3 C, 0.5 C, 0.75 C, 1.0 C, 1.5 C, 2.0 C, and 2.5 C. The voltage at each time with respect to each current value was plotted, with the horizontal axis as the current value and the vertical axis as the voltage. The slope of that curve was taken as the resistance, and the resistance at 10 seconds was taken as the overall resistance. Resistance was viewed as having these primary components: the resistance at 0.1 second (0.1-sec DCR), which was taken to be electronic resistance (Resistance A); the resistance from 0.1 to 1 second ((1-0.1)-sec DCR), which was taken to be reaction resistance (Resistance B); and the resistance from 1 to 10 seconds ((10-1)-sec DCR), which was taken to be ionic diffusion resistance (Resistance C)^{(12), (13)}.

3.3.3. Cycle test

A cycle test was conducted to evaluate cell durability. Measurements were made with the cells placed in a thermostatic chamber at 45°C, the upper voltage limit set at

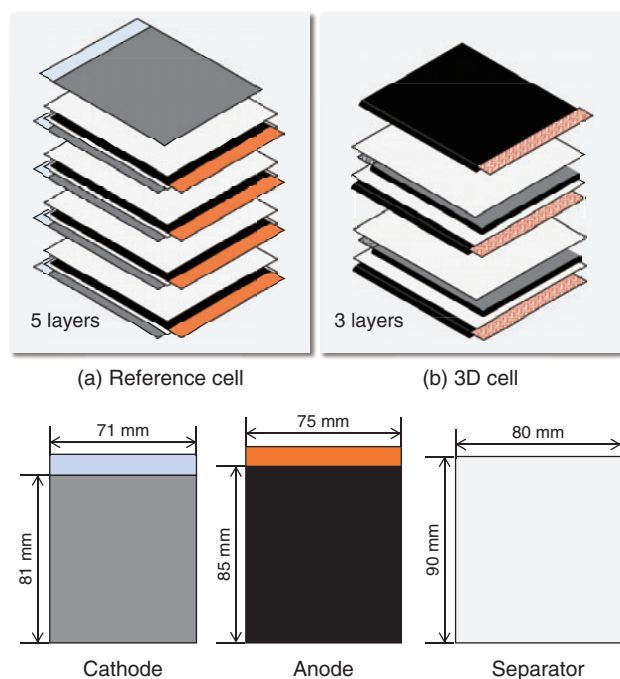


Fig. 6 Multilayer cell element

4.2 V, and the lower voltage limit at 2.5 V, and then subjected to CC discharge at 0.5 C and CCCV charging at 0.5 C for CV time of one hour and rest time of one hour. Every 200 cycles, the thermostatic chamber was set to 25°C and the capacity for the rated discharge test was confirmed. At the completion of 600 cycles, the 10-sec DCR was measured.

3.4. Analysis of Electrodes

3.4.1. SEM

Cross sections were prepared using a cross-section polisher and observed using an ULTRA 55 SEM from Carl Zeiss NTS GmbH to confirm the state of active material contact with the collector in the electrode.

3.4.2. Electron probe microanalyzer (EPMA)

Cross sections were prepared using a cross-section polisher and observed using a JXA-8500F from JEOL Ltd. to confirm the state of dispersion of each material in the electrode.

3.4.3. Pore distribution measurement

Measurements to quantify pore distribution in the electrodes were carried out by the mercury penetration method using a POREMASTER 60-GT fully automatic pore distribution measurement device manufactured by Quantachrome Instruments.

3.4.4. Scanning probe microscope (SPM)

Electrode cross sections were prepared using argon ion milling, and observed using an SFT-3500 fully automatic Nano Search microscope from Shimadzu Corporation, to quantify changes in the electron conductive paths to the active materials in the cathode before and after the cycle test. As the schematic diagram in Fig. 7 shows, each active material particle is touched with the probe, an 8-V bias voltage sufficient for stable measurement of resistance in the active materials is applied, and the resistance is calculated from the current value.

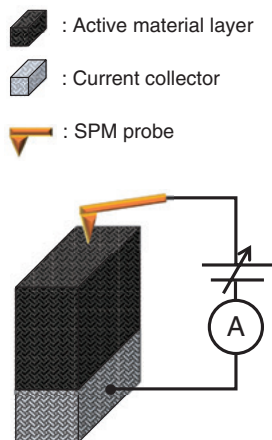
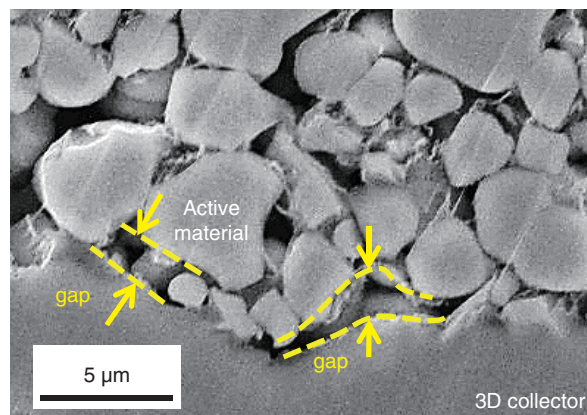


Fig. 7 Schematic diagram of SPM

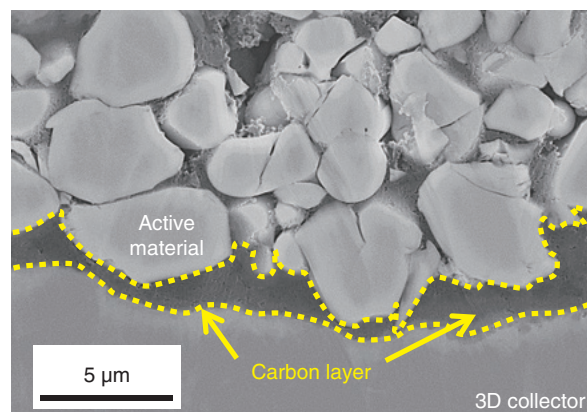
4. Results and Discussion

4.1. Results of Observation of Cathode Cross Sections

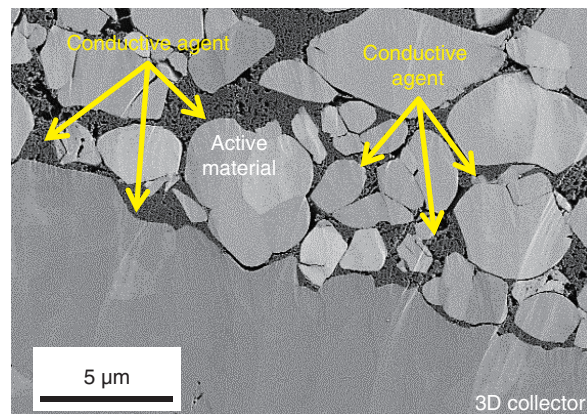
Figure 8 shows the results of observation by SEM of cross sections of (a) 3D cathode (standard), (b) 3D cathode (C coating), and (c) 3D cathode (CSB-2). Figure 9 shows the element mapping of carbon and fluorine in the 3D cathode (standard) and 3D cathode (CSB-2) observed using the EPMA.



(a) 3D cathode (standard)



(b) 3D cathode (C coating)



(c) 3D cathode (CSB-2)

Fig. 8 Cross-sectional SEM images of 3D cathodes

It is apparent from Fig. 8 that in (a) there are gaps where the active material does not directly contact the collector, and some active material is isolated. This causes an increase in electronic resistance. As the broken lines in the figure show, in (b) there is a carbon layer on the surface of the collector. Thus, it was confirmed that the active material is contacting this collector evenly through the conductive carbon layer. Consequently, enhancing the electronic conductivity between the collector and the active material can be expected to have the effect of suppressing electronic resistance in the electrode.

In Fig. 8(c) it was confirmed that the conductive agent has penetrated the gaps between the particles of active material and is well dispersed. It is thought that because the 23-nm primary particle size of the CSB-2 conductive

agent is less than half the 48-nm primary particle size of the regular AB conductive agent, its ability to fill the gaps was enhanced.

From Fig. 9, it can be confirmed that for the entire electrode, the dispersion of carbon (representing the conductive agent) and fluorine (representing the binder) is increased in (c) compared with (a). This is thought to be because the dispersion of each material was enhanced by applying the conductive agent dispersed within a solvent rather than as a powder. In light of these analysis results, it is expected that enhancing electronic conductivity within the electrode composite will reduce resistance in the electrode. In addition, it is known that because the binder used to enhance electrode binding does not itself contribute to the battery reaction, resistance will increase if dispersion

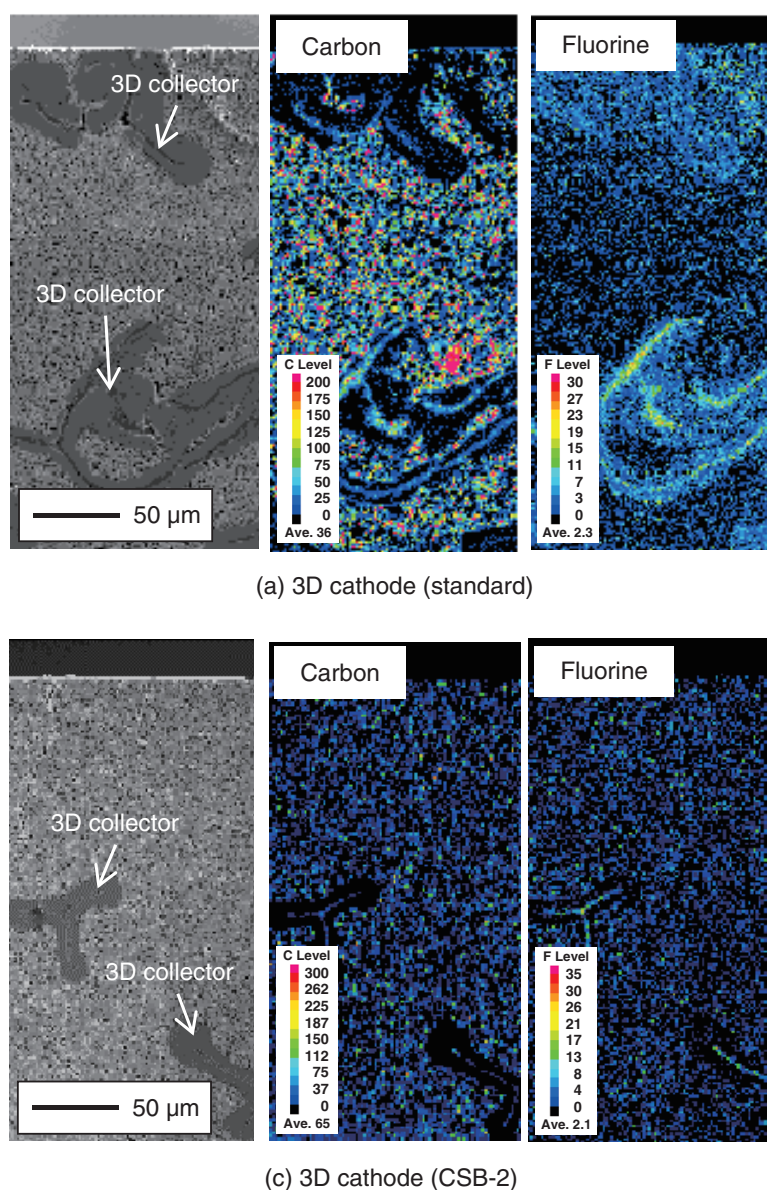


Fig. 9 EPMA elemental mapping analysis of 3D cathode

is low⁽¹¹⁾. However, increasing dispersion of the binder in (c) 3D cathode (CSB-2) can be expected to reduce reaction resistance in the electrode.

4.2. Measurement Results of Cathode Initial Resistance

Figure 10 shows the 10-sec DCR results for each cathode. This confirms that the resistance for all 3D cathodes is suppressed relative to the foil-coated cathode.

In Resistance A, the primary component of resistance is electronic resistance, and was $8.8 \Omega\cdot\text{cm}^2$ for the 3D cathode (standard) compared with $10.4 \Omega\cdot\text{cm}^2$ for the foil-coated cathode. Thus, it was confirmed that the 3D collector effectively reduced resistance by $1.6 \Omega\cdot\text{cm}^2$. Moreover, the resistance was $7.9 \Omega\cdot\text{cm}^2$ for the 3D cathode (C coating), and $7.2 \Omega\cdot\text{cm}^2$ for the 3D cathode (CSB-2), confirming that they further reduce resistance relative to the 3D cathode (standard). As was confirmed by the cross-section SEM image in Fig. 9, in the 3D cathode (C coating), it is thought that increasing the contact at the interface between the collector and active material has the effect of increasing the electronic conductivity between the active materials and the collector. In the 3D cathode (CSB-2), it is thought that the fill of conductive agent between the active materials had the effect of increasing electronic conductivity between the active materials. From these results, it was confirmed that both of these remedial measures were able to reduce electronic resistance in the electrodes.

In Resistance B, the primary component of resistance is reaction resistance, which was $1.6 \Omega\cdot\text{cm}^2$ for the 3D cathode (standard), $1.7 \Omega\cdot\text{cm}^2$ for the 3D cathode (C coating), and $0.8 \Omega\cdot\text{cm}^2$ for the 3D cathode (CSB-2), compared with $0.9 \Omega\cdot\text{cm}^2$ for the foil-coated cathode. Thus, it was confirmed

that the 3D cathode (standard) and 3D cathode (C coating) increased resistance, while the 3D cathode (CSB-2) reduced it. It is apparent from the fluorine element mapping by the EPMA in Fig. 10 that the 3D cathode (standard) contains areas where the binder has low dispersion and is unevenly distributed. This is thought to be increasing reaction resistance. The 3D cathode (C coating) uses the same slurry, and thus has a similar tendency. By contrast, because the binder in the 3D cathode (CSB-2) has been confirmed to be evenly distributed with high dispersion, this is thought to be suppressing reaction resistance in the electrode.

In Resistance C, the primary component of resistance is ionic diffusion resistance, which was $1.9 \Omega\cdot\text{cm}^2$ for the 3D cathode (standard), $1.4 \Omega\cdot\text{cm}^2$ for the 3D cathode (C coating), and $1.3 \Omega\cdot\text{cm}^2$ for the 3D cathode (CSB-2), compared with $1.7 \Omega\cdot\text{cm}^2$ for the foil-coated cathode. Thus, it was confirmed that the CSB-2 conductive agent has a considerable effect in reducing resistance. As shown by the physical properties of each conductive agent in Table 2, using the CSB-2 conductive agent increases specific surface area to $133 \text{ m}^2/\text{g}$, compared with $41 \text{ m}^2/\text{g}$ for AB. Also, the DBP absorption, which shows the penetrability of the solution, increases to $220 \text{ ml}/100\text{g}$, compared with $114 \text{ ml}/100\text{g}$ for AB. Based on this, it is thought that increasing the penetration of electrolyte solution into the pores of the electrode makes it easier to supply lithium ions to the active material, suppressing ionic diffusion resistance in the electrode.

4.3. Results of Cathode Durability Evaluation

Figure 11 shows the rate of change in capacity every 200 cycles from the cycle test at 45°C . In contrast to the foil-coated cathode, which had a capacity retention of 79% after 600 cycles, the capacity retention of the 3D cathode (standard) was 84%, the 3D cathode (C coating) 85%, and

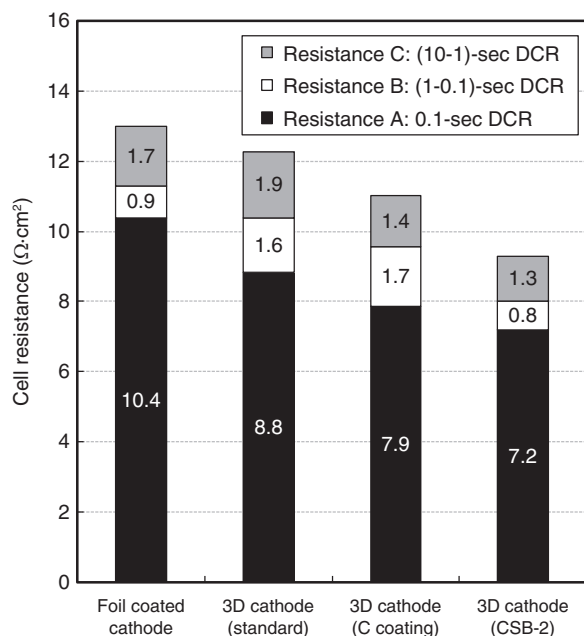


Fig. 10 Results of 10-sec DCR for cathodes

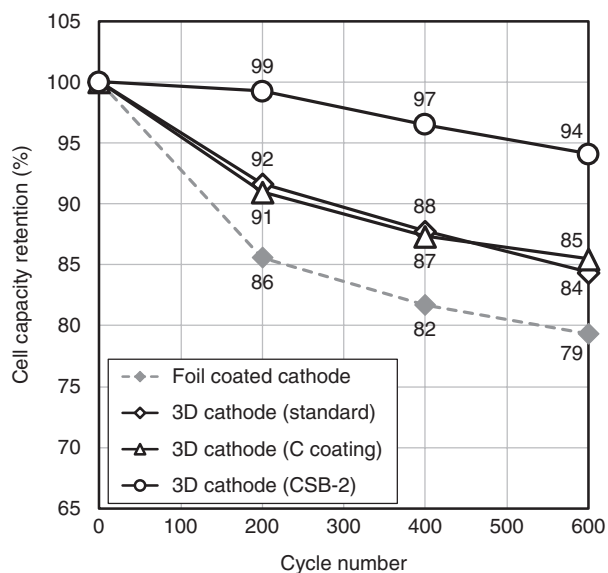


Fig. 11 Capacity retention performance of cathodes

the 3D cathode (CSB-2) 94%. This confirms that capacity retention is heightened for all 3D cathodes. This is thought to occur because the aluminum frame that forms the 3D lattice structure maintains its structure during cycle testing. Also, maintaining the binding of the various constituent materials throughout the electrode keeps the active material from detaching. The 3D cathode (C coating) increased contact between the collector and active material, with the effect of suppressing electronic resistance at their interface. However, because the frame structure of the electrode and the contents of the electrode composite were unchanged, it was equivalent to the 3D cathode (standard) with respect to capacity degradation. On the other hand, the 3D cathode (CSB-2) not only effectively suppressed deterioration of the 3D lattice structure, but the enhanced dispersive properties of the conductive agent suppressed the interruption of conductive paths between the active materials, and the enhanced ionic diffusion suppressed interruption of ion paths. These are thought to have enhanced the suppression of capacity degradation.

Figure 12 shows the change in 10-sec DCR before and after 600 cycles of the cycle test at 45°C, while Table 5 shows the values of each component of resistance. Figure 12 and Table 5 confirm that for all 3D cathodes, the increase in 10-sec DCR resistance is suppressed relative to the foil-coated cathode. For the 3D cathodes, it was confirmed that suppressing the increase in Resistance A caused the increase in overall resistance to be suppressed. Resistance A more than doubled for the foil-coated cathode following the durability test, changing from 10.4 $\Omega\cdot\text{cm}^2$ before to 26.5 $\Omega\cdot\text{cm}^2$ after. By contrast, the 3D cathode (standard) changed from 8.8 $\Omega\cdot\text{cm}^2$ to 12.3 $\Omega\cdot\text{cm}^2$, confirming that the

Table 5 Change in cathode resistance

		Reference cathode	3D cathode (standard)	3D cathode (C coating)	3D cathode (CSB-2)
Resistance A ($\Omega\cdot\text{cm}^2$)	Before	10.4	8.8	7.9	7.2
	After	26.5	12.3	8.3	8.8
Resistance B ($\Omega\cdot\text{cm}^2$)	Before	0.9	1.6	1.7	0.8
	After	4.7	5.0	4.4	3.2
Resistance C ($\Omega\cdot\text{cm}^2$)	Before	1.7	1.9	1.4	1.3
	After	3.2	2.6	2.3	1.8

increase in resistance was suppressed. Furthermore, the 3D cathode (C coating) changed from 7.9 $\Omega\cdot\text{cm}^2$ to 10.4 $\Omega\cdot\text{cm}^2$, and the 3D cathode (CSB-2) changed from 7.2 $\Omega\cdot\text{cm}^2$ to 8.8 $\Omega\cdot\text{cm}^2$, confirming an even greater effect in suppressing the increase in resistance relative to the 3D cathode (standard). Because the primary component of resistance in Resistance A is electronic resistance, it is conceivable that the aluminum frame of the 3D cathode is suppressing the increase in resistance by reducing the interruption of electron conductive paths caused by separation of the active material from the collector during cycling. It is thought that the 3D cathode (C coating) is particularly effective at suppressing the interruption of electron conductive paths, due to the tight contact between the active material and the collector imparted by the conductive carbon particles.

4.4. Results of Active Material Conductivity Evaluation

Figure 13 shows the results of the active material conductivity evaluation conducted using SPM for both the foil-coated cathode and 3D cathode (C coating) before and after 600 cycles of the cycle test at 45°C. The particles in the SEM cross-section images of each electrode are active materials. The SPM probe touched each particle of active material and applied a bias voltage of 8 V, after which the resistance was calculated based on the current value. The measured active materials were sorted into resistance values of less than 50 M Ω , 50 M Ω or more, 500 M Ω or more, and 1000 M Ω or more. Figure 14 shows a graph indicating the ratio of resistance in the active materials of each electrode. Figure 15 shows the results of measurements taken near the aluminum collector of the 3D cathode (C coating) using SPM.

From Fig. 13 and Fig. 14, it was confirmed that the ratio of active material with a high resistance in (a) the foil-coated cathode had increased following the cycle test compared with before. In short, it is conceivable that the internal structure of the electrode in (a) the foil-coated cathode, an electrode with a thickened coating, was changed with each cycle repetition. This would result in decreased electronic conductivity to the active material and increase resistance following each cycle. This result agrees with that seen in Fig. 12, where there was a large post-cycle increase in Resistance A, whose primary component of resistance is electronic resistance.

The pre/post cycle change for (b) the 3D cathode (C coating), in the 50 M Ω or more range of active materials, amounted to a marginal increase. Therefore, it was

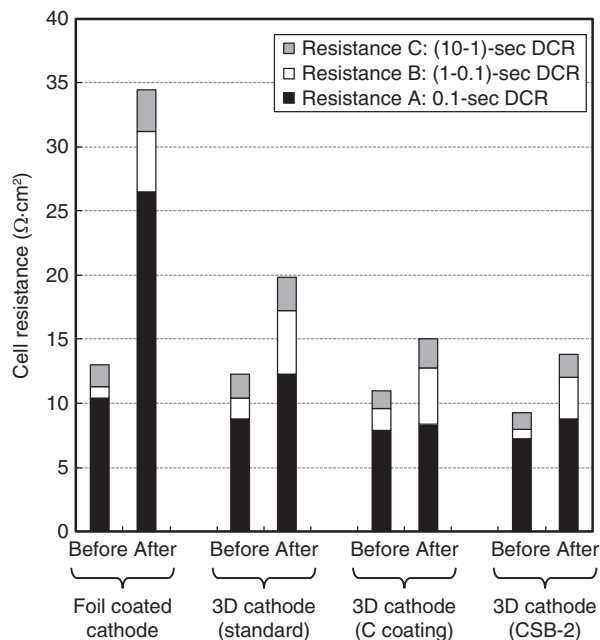
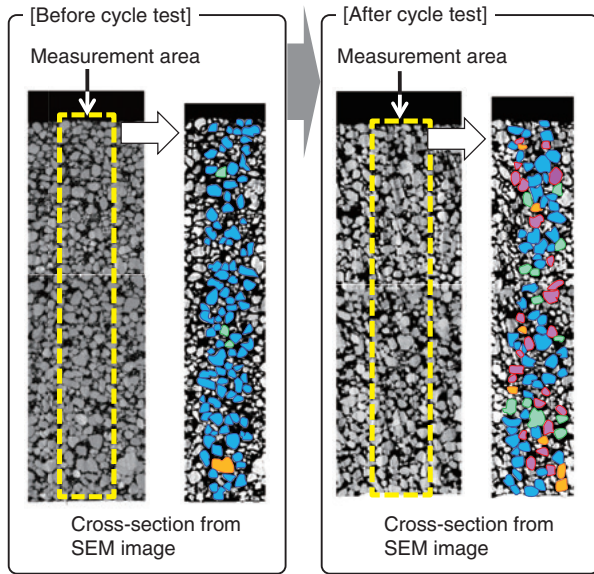
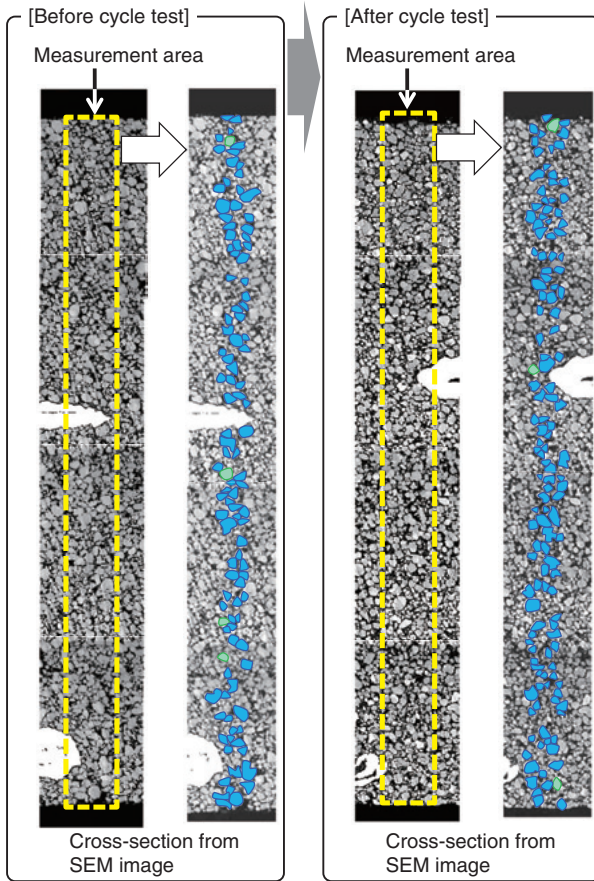


Fig. 12 Resistance performance of cathodes retention



(a) Foil coated cathode



(b) 3D cathode (C coating)

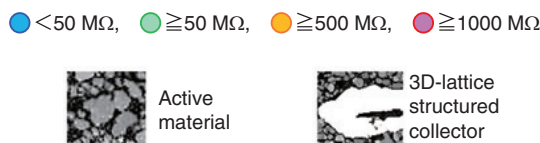


Fig. 13 Results of conductivity measurements by SPM

confirmed that there was no change in the conductivity to the active material before and after each cycle. In the 3D cathodes, the lattice-structure collectors have a constant ratio regardless of the direction of electrode thickness. Moreover, Fig. 15 confirms that the conductivity of the active materials near the collector is stable even after the durability test. In other words, even when the 3D electrodes are made thicker, the presence of the collector within the electrode suppressed structural change during each cycle. Furthermore, because there is no change in distance between the active material and the collector in the direction of thickness, it can be assumed that the interruption of electron conductive paths to the active material is suppressed. In particular, it is thought that this effect was further amplified in the 3D cathode (C coating), due to the enhanced contact between the active material and collector imparted by the carbon coating. This

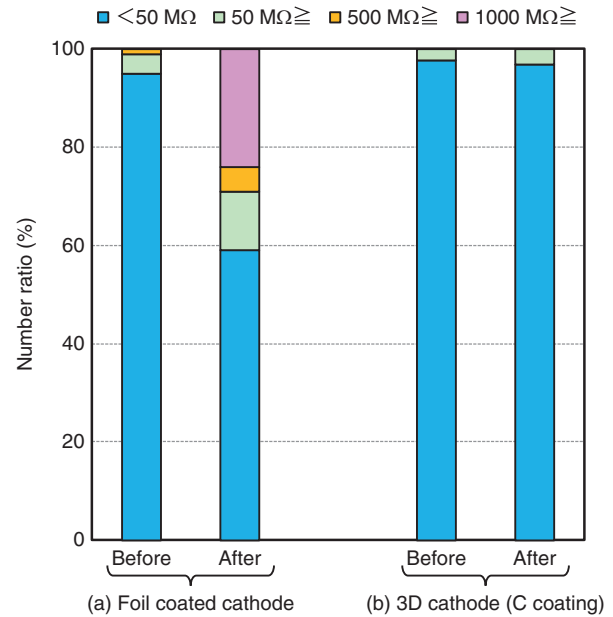


Fig. 14 Relationship between resistance and number of active materials retention

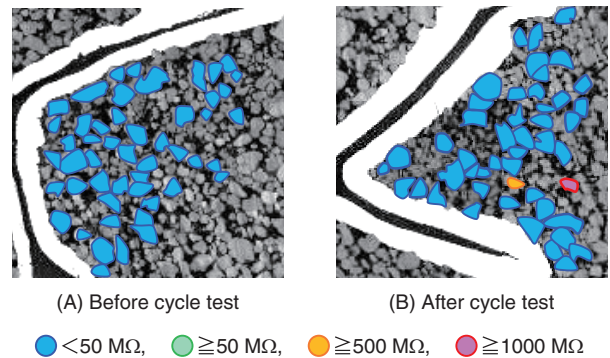


Fig. 15 Results of conductivity measurements of 3D cathode (C coating) by SPM

Table 6 Energy density of cell element

	Reference cell	3D cell
Cathode volume (mL)	4.64	4.56
Anode volume (mL)	4.38	4.52
Separator volume (mL)	1.38	0.81
Element volume (mL)	10.40	9.65
Capacity (Ah)	1.76	1.80
Cell Voltage (V)	3.62	3.61
Energy density (Wh/L)	614	674

is clearly established in Fig. 12 by the fact that the post-cycle rate of increase in Resistance A was kept to within 6%.

4.5. Laminated Cell Characteristics

Figure 16 shows the charge/discharge curve for the laminated cell rated discharge test. Table 6 shows the energy density results for each cell element calculated from this discharge capacity. The energy density per cell element for the reference cell and 3D lattice-structured electrode cell (3D cell) was 614 Wh/L and 674 Wh/L, respectively. Therefore, it is clear that using 3D collectors increases energy density by 9.8%. This shows that using 3D electrodes made it possible to increase electrode layer thickness, and decrease the number of electrode layers from 9 to 5. The result, as shown in Table 4, was a 41.7% reduction in the volume of separator used, and an increase in the ratio of active materials in the cell element, which increased energy density.

Figure 17 shows the 10-sec DCR results for each cell. The resistance was 85.1 mΩ for the 3D cell, compared with 100.5 mΩ for the reference cell, confirming a 15.4-mΩ reduction in resistance. A 24-mΩ decrease in Resistance A,

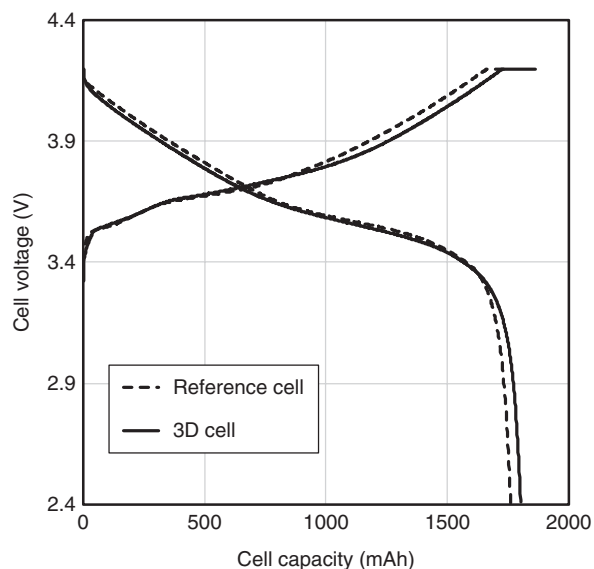


Fig. 16 Charge and discharge curves at 0.3 C

7.4-mΩ increase in Resistance B, and 1.3-mΩ increase in Resistance C were confirmed for the 3D cell with respect to the reference cell. Therefore, it was confirmed that reducing Resistance A caused a reduction in overall resistance. As was confirmed by evaluation of electrode characteristics in small cells, increasing electronic conductivity through the presence of a metal framework in the 3D electrode reduces Resistance A, whose primary component of resistance is electronic resistance. Conversely, as Fig. 8 shows, factors such as the uneven distribution of binder cause an increase in Resistance B, whose primary component of resistance is reaction resistance. In addition, because the coating thickness on one sheet of electrode is roughly double that of the reference cell, the distance ions travel is increased. This is thought to increase Resistance C, whose primary component of resistance is ionic diffusion resistance.

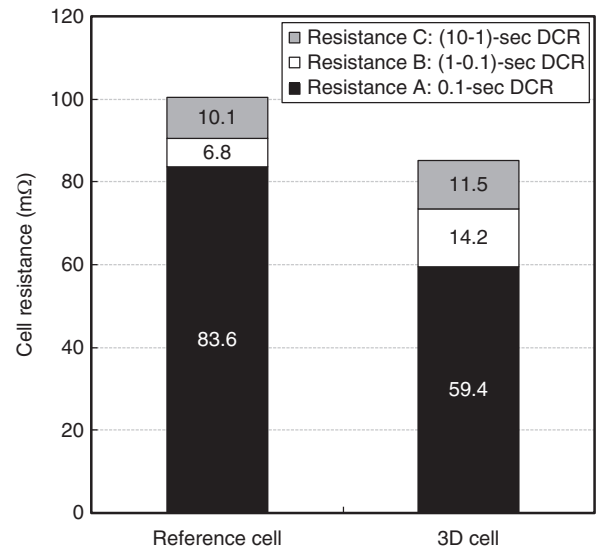


Fig. 17 Results of 10-sec DCR

5. Conclusion

Remedial measures were implemented in the application of 3D electrodes to lithium-ion batteries, and the following results were obtained.

- (1) It was confirmed that applying a conductive carbon layer to the surface of the aluminum framework allowed the active material to contact the collector evenly via the conductive carbon layer.
- (2) It was confirmed that the dispersion of each material was enhanced by applying a fine particle conductive agent dispersed within a solvent.
- (3) The results of the initial resistance measurement confirmed an inhibitory effect for each component of resistance.
- (4) The results of the durability test confirmed an effect

increasing capacity retention and suppressing increase in resistance.

- (5) Conductivity evaluations were carried out before and after the durability test, and it was confirmed that the interruption of conductive paths was suppressed in the 3D electrodes even following the durability test.
- (6) It was confirmed that the effective reduction in the number of electrode layers accompanying the enhanced loading in 3D electrodes resulted in a 9.8% increase in energy density of the cell element for a cell using 3D lattice-structured electrodes (674 Wh/L), compared with a cell using foil-coated electrodes (614 Wh/L).

The results above show that by applying 3D electrodes, it is possible to increase the energy density of lithium-ion batteries while reducing initial resistance and increasing durability.

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