Development of New Aluminum-Celmet Current Collector That Contributes to the Improvement of Various Properties of Energy Storage Devices

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The authors have developed a novel porous metal “Aluminium-Celmet” that is suitable for the cathode current collector of lithium ion batteries and other rechargeable batteries operated at a high voltage. Aluminium-Celmet features a high porosity up to 98%, large relative surface area, unique three-dimensional structure, and high corrosion resistance. In a demonstration test, the lithium ion battery using Aluminium-Celmet for its cathode current collector showed improved battery capacity, discharge property and cycle life as compared to the conventional lithium ion battery.

Keywords: porous metal, aluminium, lithium ion battery

1. Introduction

While public concern about the global environment has been growing recently and power demand is barely satisfied after the nuclear accident following the Great East Japan Earthquake on March 11, 2011, rechargeable batteries are attracting great attention and the market for them is expanding quickly. As power supplies for electric vehicles (EVs) and hybrid electric vehicles (HEVs), which have been dubbed “running rechargeable batteries,” nickel-metal hydride batteries and lithium ion batteries are common. Nickel-metal hydride batteries are especially common as power supplies for HEVs, whose demand has been increasing rapidly these days.

As the cathode current collector[*1] of nickel-metal hydride batteries, Celmet, a nickel porous material, is common and significantly contributing to increases in battery capacity[*2] and discharge property[*3(1)-(3)]. However, nickel-metal hydride batteries are expected to be replaced by lithium ion batteries as power supplies for HEVs and EVs in the future because lithium ion batteries can realize a higher energy density: Having lithium transition metal oxides, such as lithium cobalt oxides, as the cathode active material[*4] and carbon, such as graphite, as the anode active material, lithium ion batteries have a voltage rating of 3.7 V, which is far higher than that of nickel-metal hydride batteries, which is 1.2 V.

The New Energy and Industrial Technology Development Organization (NEDO) indicated in its Development of High-performance Battery System for Next-generation Vehicles project in 2008 that the target energy density of rechargeable batteries should be increased to 500 Wh/kg, which is extremely high, that is, about five times as high as today’s average density of lithium ion batteries. To achieve this target, private companies, universities and research institutes are actively committed to research and development.

The Aluminum-Celmet we recently developed is an aluminum porous material, characterized by a high porosity (up to 98%) and unique three-dimensional mesh structure. It is perfect for the cathode current collectors of many battery applications such as lithium ion batteries, capacitors, and molten salt electrolyte batteries that Sumitomo Electric Industries, Ltd. has developed, and is expected to contribute to the improvement of their performance. The theory of how Aluminum-Celmet will improve battery performance is explained below.

Aluminum foil is common as a material for the cathode current collectors of the above-mentioned batteries today. When Aluminum-Celmet is used in place of the foil, the cathode active material can be filled up to an ultimately high density level thanks to its characteristic high porosity (up to 98%), improving battery capacity. Another feature of Aluminum-Celmet is its three-dimensional mesh structure. It has spherical pores called cells, which hold the active material. As the structure encloses the material, uniform current collection from the whole active material is enabled, improving the battery discharge property.

In this present study, we used Aluminum-Celmet as the cathode current collector of lithium ion batteries, and confirmed improvement in various battery properties. This paper details the improvements.

2. Experimentation Method

2-1 Preparation of Aluminum-Celmet

Aluminum-Celmet was prepared as follows: First, plastic foam material with interconnected cells was processed to be electrically conductive. It was then provided with a specific amount of aluminum by means of our original method. The Aluminum-Celmet was completed when the plastic foam material was removed.

2-2 Corrosion resistance evaluation

We evaluated the corrosion resistance of Aluminum-Celmet in lithium ion batteries by measuring cyclic voltammetry (CV)[*5]. We prepared an electrolyte used commonly in lithium ion batteries for evaluation, by creating a solvent by mixing ethylene carbonate (EC) and diethylene carbonate (DEC) at the ratio of one to one in volume, and dissolving lithium hexafluorophosphate (LiPF6) as an electrolytic material at a rate of 1 mol/L into this solvent. Into the thus prepared electrolyte, we immersed 5 mm × 5 mm of Aluminum-Celmet as the working electrode, 10 mm × 10 mm of lithium metal foil as the counter electrode, and lithium metal foil as the reference electrode. We swept the electric potential in the voltage range of 2 V–5 V (versus Li+/Li), which includes the range applied to the cathode in lithium ion batteries, at the rate of 5 mV/s, and measured the amperage at different potentials.

2-3 Battery property evaluation

2-3-1 Preparation of a lithium ion battery incorporating Aluminum-Celmet

We prepared the cathode slurry by dissolving lithium cobalt oxides ($LiCoO_2$), which is the cathode active material, acetylene black (AB), which is the conductive agent, and polyvinylidene fluoride (PVDF), which is the binder, at the ratio of 90 wt%, 5 wt%, and 5wt% in N-methyl-2-pyrrolidinone (NMP), and mixed them. One-millimeter-thick Aluminum-Celmet, used as the cathode current collector, was filled with this slurry, dried, and rolled to have a specific thickness. For comparison with this Aluminum-Celmet cathode, we applied the cathode slurry prepared in the same manner to aluminum foil of 20 μm in thickness, and dried and rolled it to the specific thickness for use as an aluminum foil cathode.

Regarding the anode, we used nickel mesh material covered by lithium foil for discharge property evaluation, and graphite for cycle life evaluation[*6]. The size of both the cathode and anode was 30 mm × 30 mm.

As the electrolyte, EC and DEC were mixed in the ratio of one to one in volume to create a solvent, into which LiPF6 was dissolved at a rate of 1 mol/L.

As the separator, polypropylene microporous membrane of 25 μm in thickness was used.

We finished the cell for evaluation by layering one cathode sheet, one separator sheet, and one anode sheet, and inserting them into an aluminum laminate, which was filled with electrolyte.

2-3-2 Discharge property evaluation of the lithium ion battery incorporating Aluminum-Celmet

The discharge property of the single-cell battery prepared as per section 2-3-1 was evaluated according to the following conditions: It was charged at 1/8C to 4.2 V by constant-current charging (CC charging), allowing it to stand still at a constant voltage of 4.2 V for 30 minutes, given a break for 5 minutes, and discharged at the rate of 1/8C to 5C to 2.5 V by constant-current discharging (CC discharging). The capacity was evaluated at different discharge rates.

2-3-3 Cycle life evaluation of the lithium ion battery incorporating Aluminum-Celmet

The cycle life of the single-cell battery prepared as per section 2-3-1 was evaluated according to the following conditions: The cell was charged under an ambient temperature of 60°C for acceleration at 2C up to 4.1 V by CC charging, allowed to stand still at the constant voltage of 4.1 V for 30 minutes, given a break for 5 minutes, and discharged at the rate of 2C to 3.0 V by CC discharging. This cycle was repeated to evaluate discharge capacity after a different number of cycles.

3. Results and Discussion

3-1 Basic characteristics of Aluminum-Celmet

Table 1 shows the typical specifications and physical properties of Aluminum-Celmet. Compared with nickel-made Celmet, Aluminum-Celmet has a specific gravity of one-third and an electrical resistance of about one-half, enabling high conductivity, and making it highly suitable as a current collector.

Table 1. Typical Physical Properties of Aluminum-Celmet

Property item	Value
Porosity [%]	95
Average porous diameter [μm]	550
Relative surface area [m^2/m^3]	5600
Thickness [mm]	1.0
Weight per unit area of metal [g/m^2]	140
Tensile strength [MPa]	0.5
Electrical resistance [Ω·m]	3.0×10^{-6}

The corrosion resistance of Aluminum-Celmet is shown in **Fig. 1**. In the lithium ion battery, no current runs in the electric potential range of 2 V to 5 V (versus Li+/Li), which includes the range of voltage applied to the cathode having Aluminum-Celmet, indicating that Aluminum-Celmet can be used as the cathode current collector of lithium ion batteries.

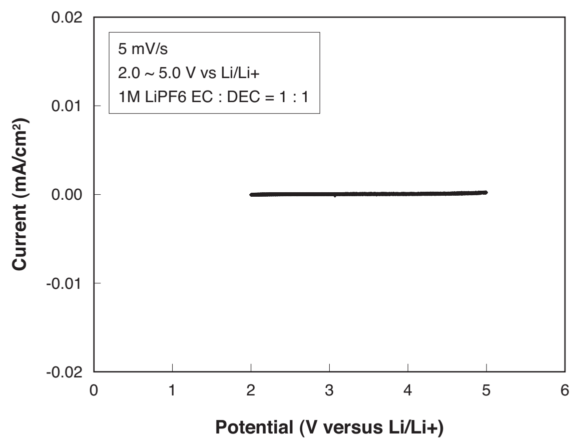

Fig. 1. Aluminum-Celmet Corrosion Resistance

3-2 Discharge property of lithium ion batteries incorporating Aluminum-Celmet

Table 2 shows the property of the single cell used to evaluate the discharge property of lithium ion batteries incorporating Aluminum-Celmet, and **Fig. 2** shows the evaluation results. If Aluminum-Celmet is used as the cathode current collector in place of aluminum foil, the cathode

Table 2. Specifications of Single Cell for Discharge Property Evaluation

Cathode	Current collector	Aluminum-Celmet electrode			Aluminum foil electrode
	Slurry mixture	$LiCoO_2$: AB : PVDF = 90 : 5 : 5 (NMP50wt%)			
	Thickness [μm]	400	160	110	120 (including Al foil 20 μm)
	Capacity [mAh/cm²]	10	4.6	2.5	2.5
Anode		Li			
Cell composition		Single side			
Electrolyte		1M $LiPF_6$ EC : DEC = 1 : 1			

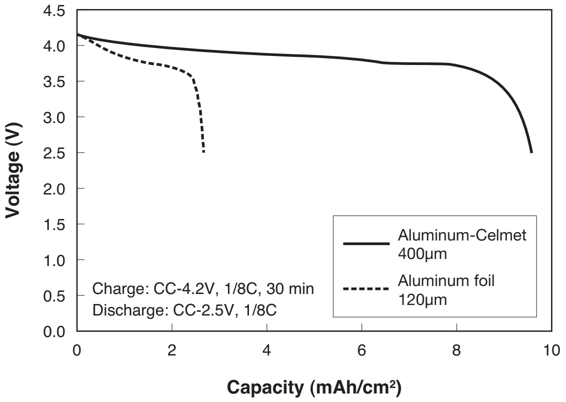

Fig. 2. Discharge Property of Lithium Ion Batteries Incorporating Aluminum-Celmet at a Charge-Discharge Rate of 1/8C

can be thickened from 120 μm to 400 μm, improving capacity in proportion to the increase in thickness. This indicates that the active material, whose amount is increased because of the increase in thickness, is thoroughly used.

Figure 3 shows the discharge rate of the single cell in the evaluation using the cathode current collector incorporating Aluminum-Celmet of different thicknesses. The evaluation indicated that when the capacity (thickness) is the same, the battery incorporating Aluminum-Celmet was superior to that incorporating aluminum foil. When the Aluminum-Celmet cathode is thicker, capacity retention of the discharge rate tended to be lower at the high discharge current density, but compared with the battery incorporating aluminum foil, the battery incorporating Aluminum-Celmet was superior in terms of capacity, irrespective of the discharge current density. This indicates that active material is held in the Aluminum-Celmet battery, and because the material is enclosed by an aluminum mesh structure, current could be collected evenly from the entire active material, and the area of contact between the current collector and active material is greater and the charge transfer resistance is lower, compared with aluminum foil.

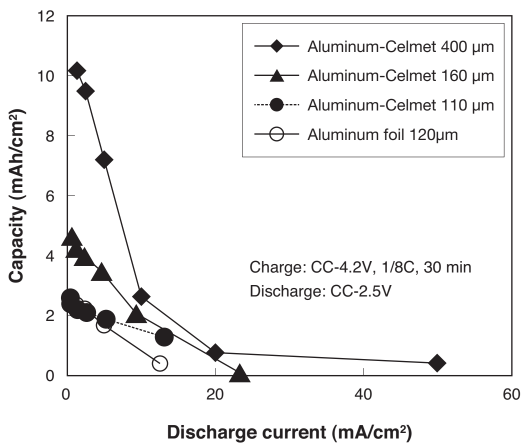

Fig. 3. Discharge Rate Property of Lithium Ion Batteries Incorporating Aluminum-Celmet

3-3 Cycle life of the lithium ion battery incorporating Aluminum-Celmet

We conducted a 60°C accelerated cycle life test of the lithium ion battery incorporating the Aluminum-Celmet as specified in **Table 3**. **Figures 4 and 5** show its discharge capacities after different numbers of charge-discharge cycles. As shown in **Fig. 4**, the battery incorporating Aluminum-Celmet has a smaller IR loss (ohmic loss) immediately after the start of discharge compared with the battery incorporating aluminum foil, which means that the internal resistance increase with the increase in the number of charge-discharge cycles can be lower. Regarding the battery capacity after 500 cycles, the capacity of both batteries was lowered by about 30% compared with the initial capacity because of the evaluation under severe conditions of charge-discharge cycles at 2C under 60°C; however, the battery incorporating Aluminum-Celmet retained a higher capacity until 500 cycles compared with that incorporating aluminum foil.

After the cycle life test, we dissembled the batteries, and reproduced single-cell batteries by combining the removed cathode and anode with lithium metal. Their specifications are shown in **Table 4** and discharge capacity evaluation results are shown in **Fig. 6**. The capacity of the battery incorporating the aluminum foil cathode after the cycle life test was about half the initial capacity, while the battery incorporating the Aluminum-Celmet cathode retained almost the same capacity as the initial capacity after the cycle life test. This means that capacity reduction of the

Table 3. Specifications of Single Cell Batteries for Cycle Life Test

Cathode	Current collector	Aluminum-Celmet electrode	Aluminum foil electrode
	Slurry mixture	$LiCoO_2$: AB : PVDF = 90 : 5 : 5 (NMP50wt%)	
	Thickness [μm]	330	110 (including Al foil 15 μm)
	Capacity [mAh/cm²]	5.5	3.0
Anode		Carbon (3.2 mAh/cm²)	
NP ratio		2.2	1.9
Cell composition		Both sides	Single side
Electrolyte		1M $LiPF_6$ EC : DEC = 1 : 1	

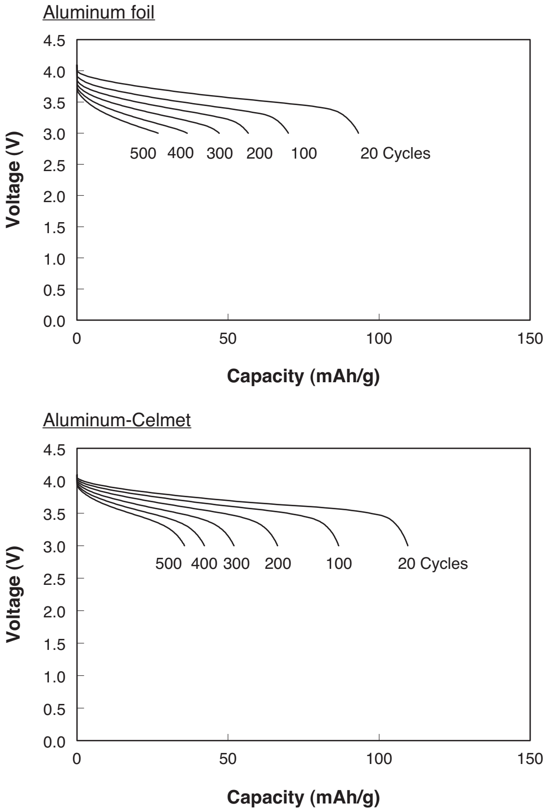

Fig. 4. Changes in the Discharge Capacity of Lithium Ion Batteries Incorporating Aluminum-Celmet under 60°C after Different Numbers of Charge-Discharge Cycles

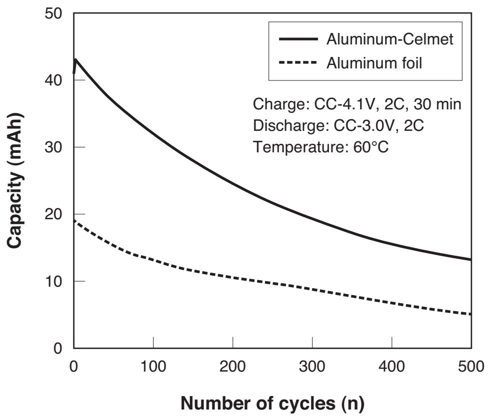

Fig. 5. Change in the Capacity of Lithium Ion Battery Incorporating Aluminum-Celmet under 60°C

battery incorporating Aluminum-Celmet after the cycle life test was mainly because of the deterioration of the anode, and the deterioration of the Aluminum-Celmet cathode was negligible. The difference can be attributed to the fact that, in the case of the aluminum-foil cathode, active material was partially removed from the aluminum foil as the active material expanded and contracted, and part of the active material deteriorated by local current concentration, resulting in a significant capacity reduction. On the other

Table 4. Specifications of the Single Cell for Discharge Capacity Evaluation Used for 60°C Cycle Life Test

Cathode	Current collector	Aluminum-Celmet electrode	Aluminum foil electrode
Cathode	Slurry mixture	$LiCoO_2$: AB : PVDF = 90 : 5 : 5 (NMP50wt%)	
Cathode	Thickness [μm]	330	110 (including Al foil 15 μm)
Cathode	Capacity [mAh/cm²]	5.5	3.0
Anode		Li	
Cell composition		Single side	
Electrolyte		1M $LiPF_6$ EC : DEC = 1 : 1	

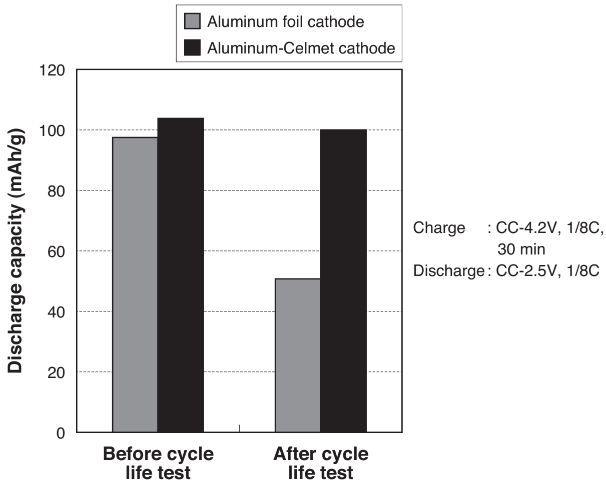

Fig. 6. Changes in Discharge Capacity of the Lithium Ion Battery Incorporating Aluminum-Celmet before and after Cycle Life Test at 60°C

hand, when Aluminum-Celmet was used as the cathode current collector, active material was retained in the cells and was not detached easily, and because active material was enclosed by the aluminum mesh structure, current was collected evenly from the entire active material, reducing active material deterioration due to locally concentrated current, thus retaining almost the same capacity after the cycle life test as the initial capacity.

4. Conclusion

We developed Aluminum-Celmet as a cathode current collector highly suitable for rechargeable batteries having high operating voltage, such as lithium ion batteries. Aluminum-Celmet has sufficient corrosion resistance in lithium ion batteries, and because of its high porosity (up to 98%), which is one of its strengths, active material filling density is improved, contributing to an increase in battery capacity. The three-dimensional mesh structure, which is another strength of the newly developed material, expands the relative surface area and enhances the active material retention effect, contributing to an improvement in the battery output property and an extension of the cycle life. From these results, the use of Aluminum-Celmet is expected not to be limited to lithium ion batteries but also can be used in capacitors and molten salt electrolyte batteries.

· Celmet and Aluminum-Celmet are trademarks or registered trademarks of Sumitomo Electric Industries, Ltd.

Technical Terms

*1 Current collector: Material used to extract electricity in batteries. Generally, cathode current collectors of lithium ion batteries use aluminum foil, and anode current collectors use copper foil.

*2 Capacity: One of the properties of battery performance, which indicates the amount of energy stored in batteries. For use in EVs, the greater the capacity, the longer the cruising distance per full charge.

*3 Output property: One of the battery performance factors. The greater the output property, the greater the current that can be extracted at any one moment. In terms of use in EVs, the greater the output property, the superior the starting (acceleration) performance.

*4 Active material: In batteries, the material that stores electricity. Generally, the cathode active material in lithium ion batteries uses lithium transition metal oxides such as lithium cobalt oxides, and the anode active material is carbon such as graphite.

*5 Cyclic voltammetry (CV): The most basic and common measurement method in the electrochemical field. It sweeps the potential of electrodes linearly and measures response current.

*6 Cycle life: One of the battery performance factors that indicates battery life. A battery with good cycle life indicates a lower capacity reduction after repeated charging and discharging, realizing a long life.

References

(1) S. Inazawa and M. Majima, SEI Technical Review No.71, pp.23-30 (2010)

(2) M. Honda, Materia Japan vol.38, No.6, pp.470-474 (1999)

(3) T. Tanigawa and K. Gomikawa, Matsushita Technical Journal vol.44, No.4, pp.419-425 (1998)

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