

Aluminum-Celmet—Aluminum Porous Metal with Three-Dimensional Consecutive Pores

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Celmet is a material that has a high porosity and a large surface area. Sumitomo Electric Toyama Co., Ltd. has offered nickel and nickel-chromium alloy Celmets. There has been a demand for aluminum porous metal due to advantages such as the light weight, thermal conductivity, and high voltage resistance. Therefore, we worked on the development of Aluminum-Celmet and succeeded in its production. This paper presents the physical properties, machine properties, and electric characteristics of the Aluminum-Celmet. We also report on the application of Aluminum-Celmet to a lithium ion battery.

Keywords: plating, molten salt electrolysis, aluminum, porous structure, battery current collector

1. Introduction

Celmet is a porous metal with a three-dimensional mesh structure. Sumitomo Electric Toyama Co., Ltd. (Sumitomo Electric Toyama) currently mass-produces Celmet in nickel and in a nickel-chromium alloy. Utilizing its characteristic of having a significantly high surface area compared with its volume, along with a high porosity of up to 98%, Celmet is used as a current collector*¹ in nickel-hydrogen batteries, catalyst carriers, electromagnetic shielding materials, filters, and as a component in fuel batteries. In order to expand usage and our Celmet lineup, we have developed an aluminum version of Celmet—Aluminum-Celmet.

Table 1 compares the characteristics of nickel and aluminum. Compared to nickel, aluminum is characterized by its lower specific gravity, lower electrical resistivity, and higher heat conductivity. Also, aluminum does not dissolve in high action potential levels in non-aqueous electrolyte solutions such as in lithium-ion batteries (LIB). This is why aluminum foil is used as the cathode collector. Utilizing these features, porous aluminum can contribute to the weight reduction of component materials, and improvement of heat transfer and performance quality of LIBs.

Although various developmental attempts have been made to date, porous aluminum is not widely available as an industrial product due to difficulties in the manufacturing processes. For example, aluminum casting,⁽¹⁾ in

which melted material is poured into a plaster mold, is not suitable for manufacturing long items and is costly. Sintering,⁽²⁾ another aluminum piece production method that uses aluminum powder, cannot deliver sufficiently high porosity and purity to the final product. To address such issues, we focused on aluminum plating. Plating is widely used for our mass-production Nickel Celmet, and if we could plate aluminum, we should be able to produce long aluminum pieces while meeting the porous metal requirements, including porosity and ductility. This paper discusses a new production method for porous aluminum utilizing plating. The features of the product and its benefits when utilized in LIBs, are also discussed.

2. Celmet Production Method and Challenges

Figure 1 shows the Celmet production method. The first step is to apply carbon paint onto an open-cell urethane foam to make the foam surface conductive. Secondly, nickel is electroplated onto the carbon painted foam to create a specified thickness of nickel substrate. The nickel plated foam is then heated to 800°C to remove the urethane. However, because this process oxidizes the nickel, the structure is then exposed to a hydrogen gas atmosphere at 1,000°C for nickel oxygen reduction. In this way, Celmet can be created using any metal—as long as it can be plated. In other words, we cannot create Celmet with metals that are unsuitable for plating. Plating usually requires an aqueous solution, however, as shown in Fig. 2,

Table 1. Nickel and Aluminum Comparison

	Nickel	Aluminum
Specific gravity	8.9 g/cm ³	2.7 g/cm ³
Electrical resistivity	69.3 nΩ·m	28.2 nΩ·m
Thermal conductivity	90.9 W/(m·K)	237 W/(m·K)
Melting point	1455°C	660°C
Oxidation	Oxidized at high temperature Reducible in hydrogen etc.	Thin and dense oxidation film Irreducible in hydrogen
Durability in non-aqueous batteries	Melts at 4.2 V (Li/Li ⁺)	No melting at 4.5 V (Li/Li ⁺)

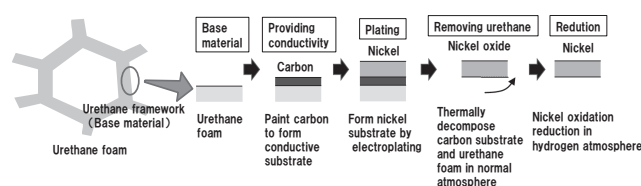


Fig. 1. Celmet Production Procedure

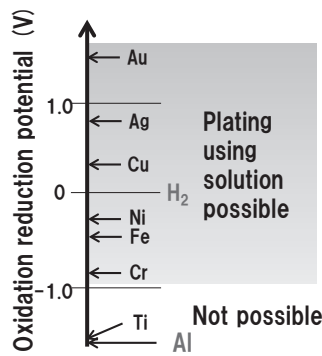


Fig. 2. Possibility of Plating Using Metal Solutions

because aluminum has a low oxidation-reduction potential, electrolysis of water starts first. For this reason, aluminum is usually classified as unsuitable for plating.

Therefore, we needed to consider a method to form an aluminum substrate with something other than an aqueous solution. Also, the oxidized aluminum is very stable and irreducible. Therefore, unlike nickel, we needed to find a way to remove the urethane foam and avoid aluminum oxidation.

3. Development of Aluminum Plating Technology

As mentioned above, plating using aqueous aluminum solution is not possible. Rather than an aqueous solution, an aluminum substrate can also be formed using either a gas-phase method, such as sputtering or vapor deposition, or the hot-dip coating method in which a base material is immersed in melted aluminum. Challenges in using the gas-phase method include the difficulty of creating a thick substrate and the impracticality of creating the substrate in the foam interior. The challenge of the hot-dip coating method is that urethane foam is dissolved in the melted aluminum, which is at a temperature of 660°C or higher. At this point, we decided to search for an aluminum plating method utilizing a non-aqueous aluminum solution working around the above challenges. Table 2 lists potential solutions. These include a molten salt solution,⁽³⁾ which is a mixture of salt of alkali metals and aluminum chloride (AlCl₃); and an organic solution, such as aluminum chloride-dimethylsulfone (DMSO₂-AlCl₃).⁽⁴⁾ However, as both

Table 2. Features of Different Aluminum Solutions

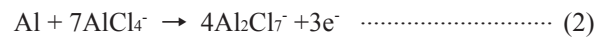
Types	Molten salt	Organic solvent	Ionic liquid
Composition	NaCl-KCl-AlCl ₃	DMSO ₂ -AlCl ₃	EMIC-AlCl ₃
Plating temperature	200°C or higher	90-180°C	Room temperature to 200°C
Surface roughness	Rough	Controllable by additives	Controllable by additives
Impurities	Fe	Fe, S, Cl	Fe
Viscosity	High	High	Low (20 cP @ 25°C)

EMIC : 1-Ethyl-3-methylimidazolium chloride
DMSO₂ : Dimethyl sulfone

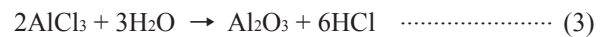
solutions need to be at a temperature of more than 90°C for plating, the urethane foam would be deformed when immersed in the solution.

We realized the possibility that aluminum chloride solution in ionic liquid,^{*2} which is a type of molten salt that is in a liquid state at room temperature (around 25°C), could be used for plating on the urethane foam. As a result of our research, we chose an ionic liquid⁽⁵⁾ in which 1-ethyl-3-methylimidazolium chloride (EMIC) and AlCl₃ are mixed at a molar ratio of 33:67 as the aluminum plating solution. EMIC was chosen because it has the highest electrical conductivity and a low melting point among the different types of aluminum ionic liquid.

In this solution, aluminum is separated at the cathode by the reaction shown in Eq. (1) below, and it is also dissolved at the anode by the reaction shown in Eq. (2). Thus, the solution composition remains constant.



However, EMIC-AlCl₃ ionic liquid displays high reactivity with water as shown in Eq. (3) and reacts even with moisture in the air to produce HCl gas, along with Al₂O₃ through the hydrolysis of AlCl₃.



Also, oxygen in the liquid causes the immediate oxidation of the formed aluminum substrate, deteriorating the plating quality. Therefore, plating must be performed in an atmosphere of a dry inert gas. Figure 3 shows the setting of our experimental aluminum plating.

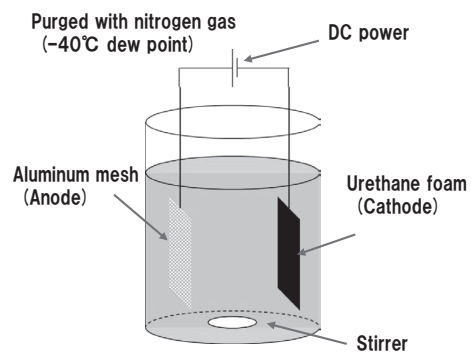


Fig. 3. Aluminum Plating Experiment Diagram

This experiment was performed in a globe box purged with nitrogen gas with its temperature controlled to remain at a dew point of -40°C or lower. Aluminum solution was poured into a glass beaker, and a piece of aluminum mesh was set to the anode and a piece of urethane foam coated with carbon was set to the cathode. The electroplating process was conducted while stirring the solution.

As a result, aluminum substrate was formed on the

surface of the urethane foam. An SEM*³ image of the plated aluminum substrate is shown in Photo 1.

Although we successfully created the plated aluminum substrate, it was fragile and crumbled during the process of washing and drying. We assumed the cause of this crumbliness was because the substrate did not form as a dense film but as a group of grains, as shown in Photo 1. We then considered the use of an additive that is also used in aqueous solution plating to create a denser film. Referring to the chemicals used as additives to aluminum-based ionic liquid, we researched various substances, including organic solvents,⁽⁶⁾ metallic ions,⁽⁷⁾ and organic materials.⁽⁸⁾ We finally discovered that adding a small amount of phenanthroline*⁴ to the aluminum solution created a smooth aluminum substrate on the surface of the urethane foam and this substrate retained its shape without crumbling (Photo 2).

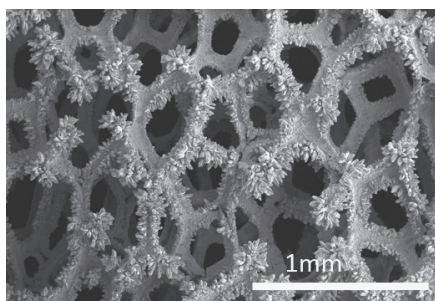


Photo 1. SEM Image of Plated Aluminum Substrate

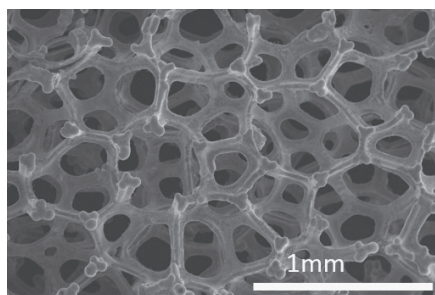


Photo 2. SEM Image of Plated Aluminum Substrate with Additive

4. Urethane Foam Removal Method

To obtain Celmet from the unfinished piece, the base urethane foam and conductive carbon coating must be removed by thermal decomposition. Figure 4 summarizes the changes in the status of the urethane foam, carbon, and aluminum at different temperatures. Thermal decomposition must be carried out at temperatures less than 660°C, the melting point of aluminum. At the same time, the temperature when carbon vaporizes as CO₂ by oxidation is 500°C or higher. Thus, the removal process must be performed within an oxygenated atmosphere at a temperature of between 500 and 660°C.

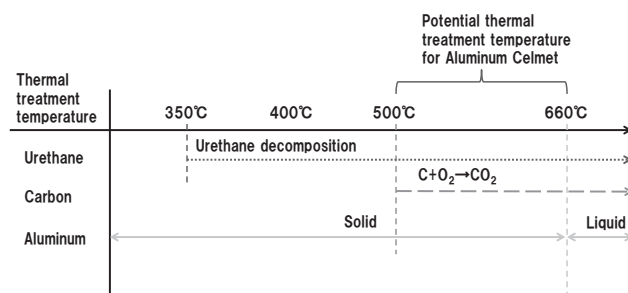


Fig. 4. Temperatures Required for Thermal Treatment of Aluminum-Celmet

Aluminum oxidation must also be taken into account when determining the optimum temperature. As mentioned earlier, it is extremely difficult to thermodynamically reduce the oxidized surface of aluminum; therefore, conditions that prevent aluminum oxidation are essential.

We eventually obtained the optimum conditions for the thermal base removal process and this optimized process successfully removed the urethane foam and carbon paint without excess oxidation of the aluminum surface. The Aluminum-Celmet thus produced had good flexibility and was bendable as shown in Photo 3.

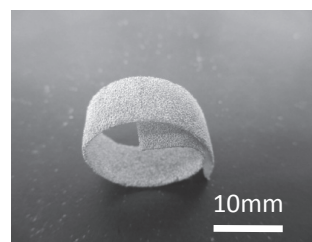


Photo 3. Flexibility of Aluminum-Celmet

5. Features of Aluminum-Celmet

5-1 Physical Properties of Aluminum-Celmet

Table 3 lists the physical properties of the developed Aluminum-Celmet. Tensile strength and electrical resistivity were measured using a test piece of 20 mm x 70 mm in size. The tensile strength was determined from the stress-strain curves obtained from a tension test with a 30 mm chuck distance and 1.0 mm/min pulling speed. Electrical resistivity was measured using the four point probe method.

Table 3. Physical Properties of Aluminum-Celmet

Thickness (mm)	Average pore diameter (μm)	Plating density (g/m ²)	Tensile strength (MPa)	Electrical resistivity (μΩ·m)
0.8	450	112	0.65	2.0
1	550	100	0.50	1.8
1	550	140	0.80	1.5
2	900	280	0.51	2.4

The thickness and pore diameter can be controlled by the plating conditions, while the coating density is controlled by the applied current. These conditions can be used to design the product according to its purpose.

5-2 Physical Properties of Aluminum-Celmet

This section reports the SEM observation results concerning the structural surface and cross-section of 1-mm thick Aluminum-Celmet with 550 μm pores and 140 g/m^2 density.

Photo 4 presents the surface of the structure. We confirmed that the aluminum was evenly coated throughout the structure. Also, the surface was smooth. Figure 5 shows a cross-section view. We confirmed that the aluminum substrate was sufficiently formed around the interior structure of the urethane foam.

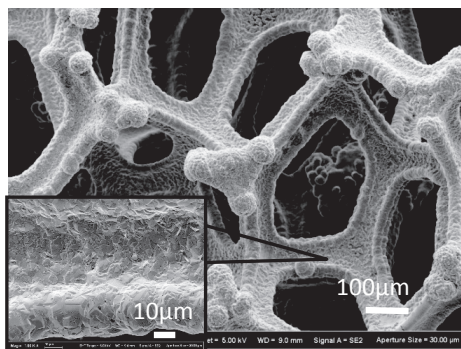


Photo 4. Aluminum-Celmet Structure

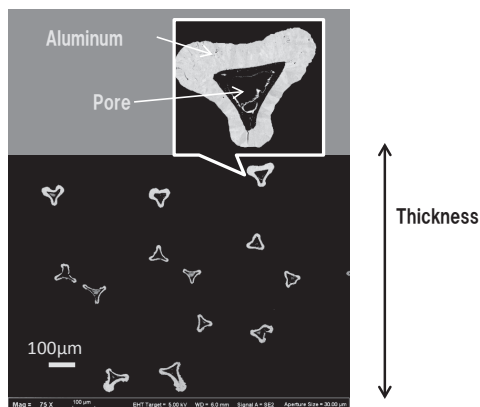


Fig. 5. Cross-Section View of Aluminum-Celmet

Photo 5 represents the crystalline structure of the aluminum plating. This is an observation made using a low voltage SEM with 5 kV of accelerating voltage, on the same sample as used for the cross-section view shown in Fig. 5 after polishing with a cross-section polisher (CP).⁵ Aluminum-Celmet crystal is characterized by its fine pillar structure despite having undergone thermal processing.

Although the ICP-MS⁶ analysis results showed the existence of Fe, Si, Cr, Mn, and Zn, the product's aluminum purity was proven to be 99.9% or higher.

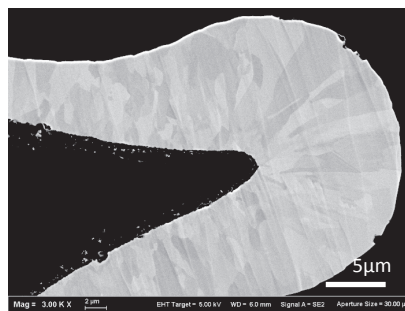


Photo 5. Aluminum-Celmet Cross-Sectional Crystalline Structure

6. Aluminum-Celmet Applications

6-1 Examples of Aluminum-Celmet Applications

Possible applications of Aluminum-Celmet are listed in Table 4, taking account of its unique structure as a Celmet, as well as the aluminum-derived features, such as high thermal conductivity, high electrical conductivity, and light weight. Out of these various applications, this section discusses applicability as the cathode collector in the LIB.

Table 4. Aluminum Celmet Applications

Feature	Use
High thermal conductivity	Heat transfer fin (air conditioners, cars) Heat sink (electronic devices)
High electrical conductivity	Current collector for power storage devices (LIBs, capacitors)
Electromagnetic wave shielding	Electromagnetic wave shields
Catalyst carrier	Optocatalytic carriers Oxidation catalytic carriers
Light weight	Light weight frames
Filtering	Various filter materials

6-2 Application to Lithium Ion Batteries

If Celmet is used as a current collector in a battery, it can retain the active material within its 3D mesh structure in a uniform manner regardless of the thickness of the electrode, which in turn increases the battery's capacity. In a nickel-hydrogen battery, Nickel-Celmet is used as the cathode collector, contributing to capacity increase in the battery. However, the LIB uses a non-aqueous solution and a high voltage is applied to the cathode. As this would cause nickel to melt into the solution, nickel cannot be used as the cathode in the LIB. In contrast, aluminum is passivated, and therefore it is not dissolved in an electrolyte. This is why aluminum foil is suitable for use as the cathode in the LIB. If we could use Aluminum Celmet in the LIB, we can expect it to increase capacity and improve the cycle characteristics, just as Nickel Celmet achieves in a nickel-hydrogen battery. To appraise this applicability of Aluminum-Celmet to LIBs, we confirmed the points shown in Table 5. We also show the voltage resistance of Aluminum-Celmet in Fig. 6.

Between 3 and 4.5 V (vs. Li/Li) applied to the LIB anode, no dissolving current occurred, confirming that we can use Aluminum-Celmet as the LIB cathode collector.

Table 5. Aluminum-Celmet/LIB Applicability Checklist

Item	Requirement	Verification method
High voltage corrosion resistance	No dissolution occurs between 3 to 4.5 V (vs. Li+/Li)	Checked no dissolution occurred at specified voltage using electrochemical measurement method
Cathode discharge capacity	Capacity equivalent to cathode using aluminum foil collector	Discharge capacity confirmed for LIB with Aluminum Celmet collector
Capacity increase	Capacity per active material unit weight is constant when active material density is high	Discharge capacity confirmed with LIB with different active material densities

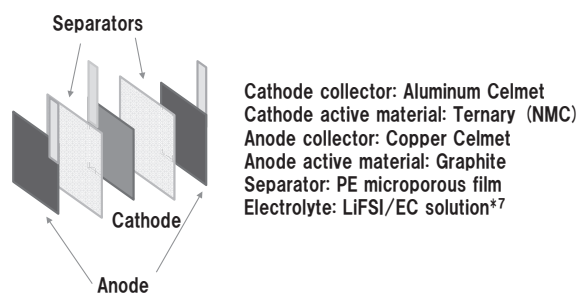


Fig. 7. Structure of Test LIB

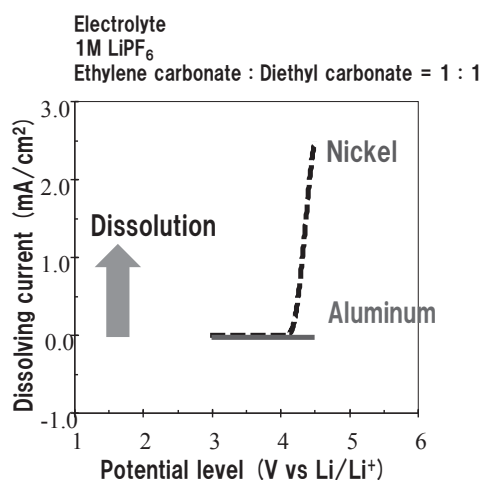


Fig. 6. Voltage Corrosion Resistance of Aluminum-Celmet and Nickel Celmet

Based on this result, we constructed a laminate cell as shown in Fig. 7 to verify that the LIB battery could use Aluminum-Celmet for the cathode. The electrode size was 5 cm x 5 cm.

The LIB charge and discharge curves obtained in this verification test are shown in Fig. 8. The discharge capacity at 0.1C in the Aluminum-Celmet LIB was 123 mAh/g. As the discharge capacity of the aluminum foil LIB is 120 mAh/g, we confirmed that we could secure comparable capacity to the LIB with an aluminum foil collector.

We also created LIBs with different active material densities in the Aluminum-Celmet electrode. Figure 9 shows the plot of discharge capacities at 0.1C for different active material densities. The reference line shows the discharge capacity per active material density when using an aluminum foil electrode with a discharge capacity of 120 mAh/g. The discharge capacities per increasing active material density in the Aluminum-Celmet electrode remain on this reference line and demonstrate that the discharge capacity per physical weight does not deteriorate even if the active material density is increased.

In other words, using Aluminum Celmet as an electrode can increase the active material density—the amount of active material per unit space—compared to an aluminum foil electrode. As this can decrease the number of electrode substrates, it is also possible to reduce components that do not directly contribute to power generation, such as separators, while also increasing battery capacity.

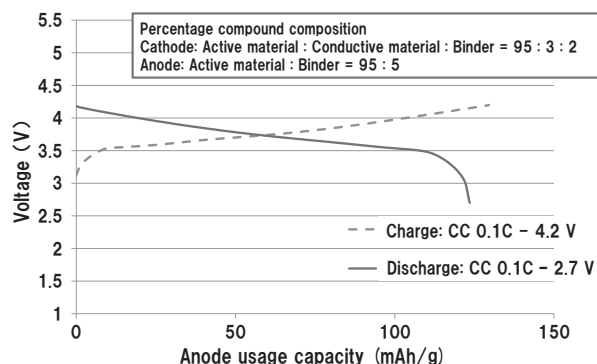


Fig. 8. Charge/Discharge Curves

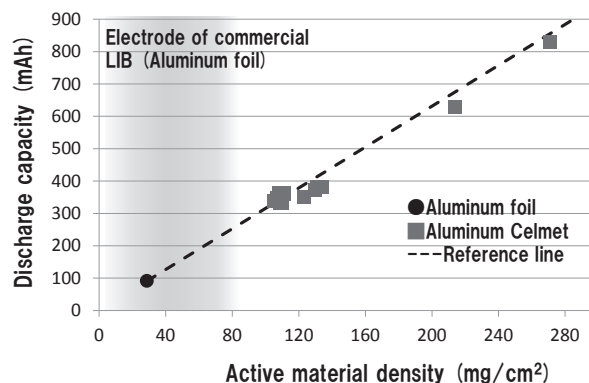


Fig. 9. Correlation Between Active Material Density and Discharge Capacity

7. Conclusions

A wide range of applications for Aluminum-Celmet is expected, for its Celmet-specific nature offering a 3D mesh structure, as well as the aluminum-derived features of being light in weight, and having high thermal conductivity and corrosion resistance at high voltage. We have developed an aluminum plating technology, which has been difficult to achieve to date, and we successfully created Aluminum-Celmet by optimizing the thermal processing conditions. The product already enjoys a number of inquiries and it is gaining a reputation in different areas of the industry. We will now focus on the development of roll-to-roll*⁸ manufacturing technology with mass-production in view. We will also develop other technologies to control

porosity, pore diameter, and thickness in order to enhance the Aluminum-Celmet lineup.

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

Technical Terms

- *1 Current collector: Material to collect an electrical current in batteries. Generally in lithium ion batteries, aluminum foil is used as the cathode collector and copper foil is used as the anode collector.
- *2 Ionic liquid: Refers to chemical compounds (salts) formed by ionic bonds and in a liquid state at room temperature.
- *3 SEM: Abbreviation for Scanning Electron Microscope. Observations are made by detecting secondary electrons emitted from the observing object through the projection of an electron beam.
- *4 Phenanthroline: A heterocyclic organic compound that contains nitrogen. Often used as an indicator for titrimetric analysis of iron.
- *5 Cross section polisher (CP): Produces smooth cross-sections of a material using an ion beam to prepare for SEM observation or other purposes.
- *6 ICP-MS: Inductively Coupled Plasma Mass Spectrometry. Using plasma as the ion source, the ions generated from the plasma are detected in the mass spectrometry analyzer chamber.
- *7 LIFSI/EC solution: Ethylene carbonate (EC) organic solvents that dissolve lithium bis (fluorosulfonyl) imide.
- *8 Roll-to-Roll manufacturing: An efficient manufacturing method to produce an item in a rolled sheet format by continuously processing it between two moving rolls.

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