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(57) **ABSTRACT**

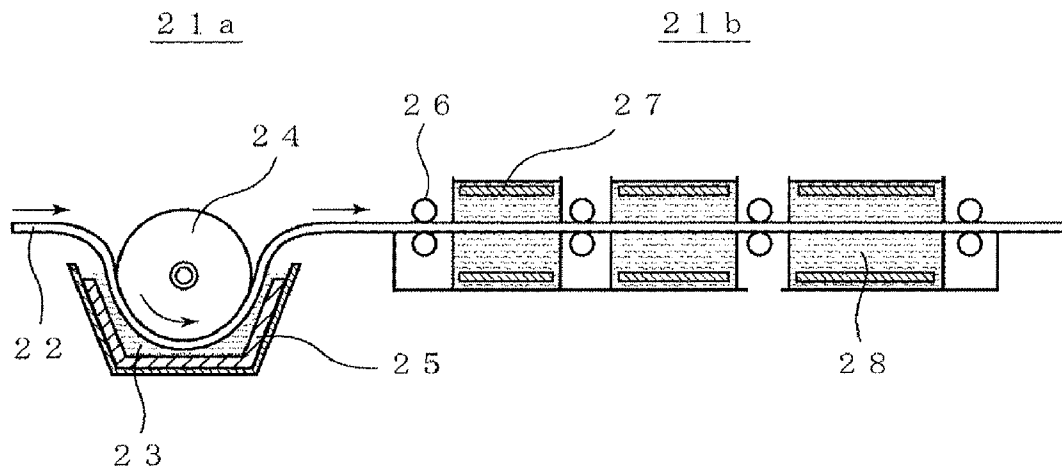
A surface of a porous resin body having a three-dimensional network structure can be plated with aluminum at a uniform thickness and thus a high-purity aluminum structure is formed. A method for producing an aluminum structure includes a step of plating a resin porous body, which has a three-dimensional network structure and has a surface that has been made electrically conductive, with aluminum in a molten-salt bath, in which the molten salt is a salt mixture of aluminum chloride and an organic salt and plating is conducted while controlling the temperature of the molten-salt bath to be 45° C. or higher and 100° C. or lower. Preferably, the molten-salt bath further contains 1,10-phenanthroline at a concentration of 0.25 g/l or more and 7 g/l or less.

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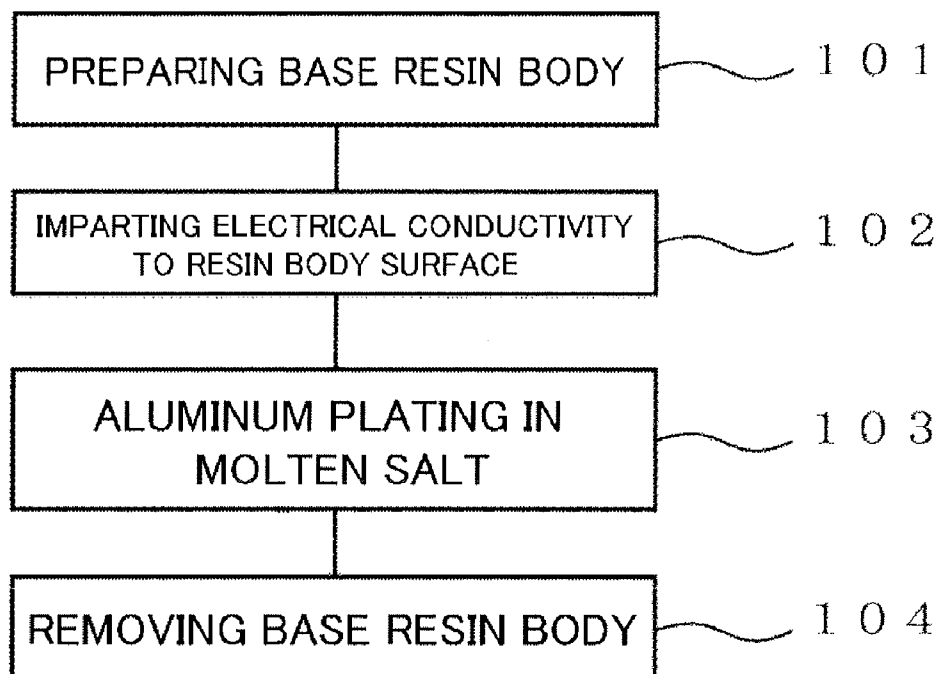
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### Related U.S. Application Data

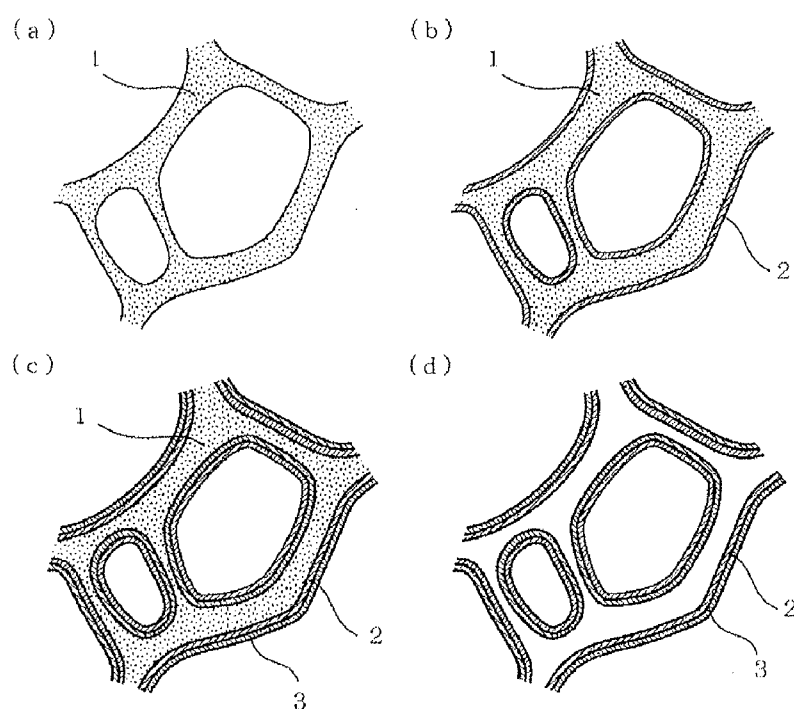
(63) Continuation of application No. PCT/JP2012/050130,  
filed on Jan. 6, 2012.



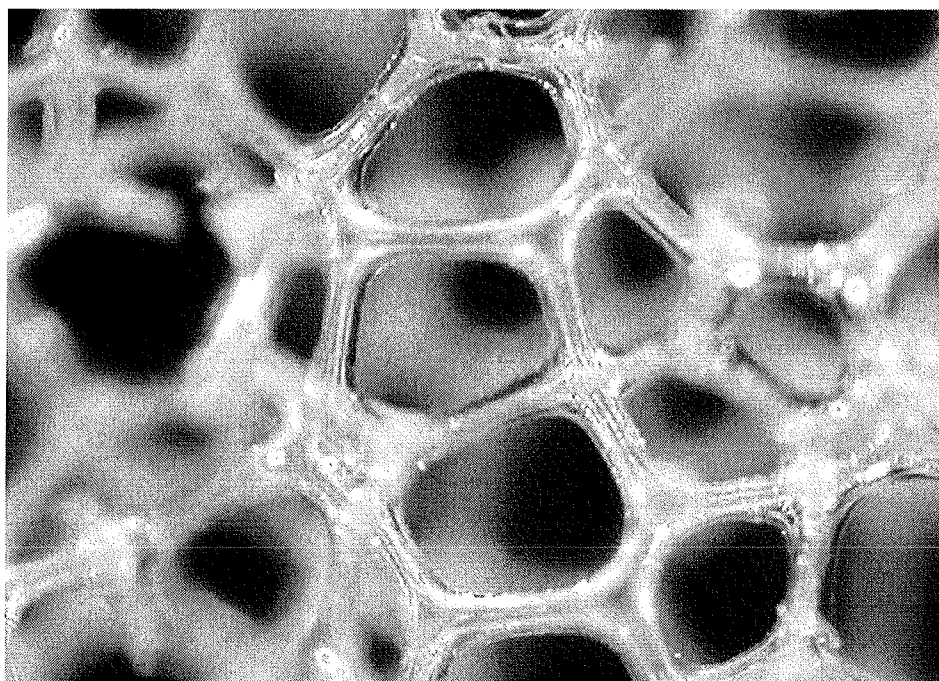
**FIG. 1**



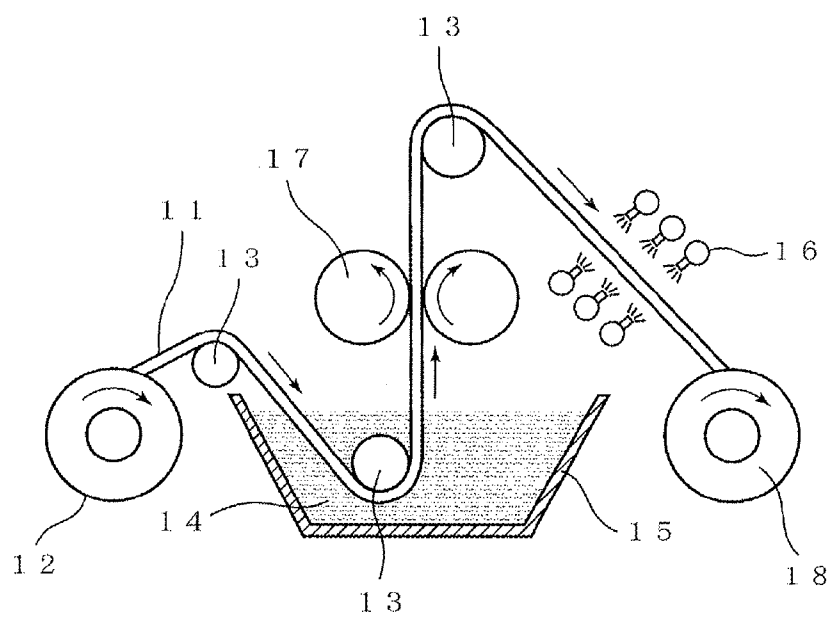
**FIG. 2**



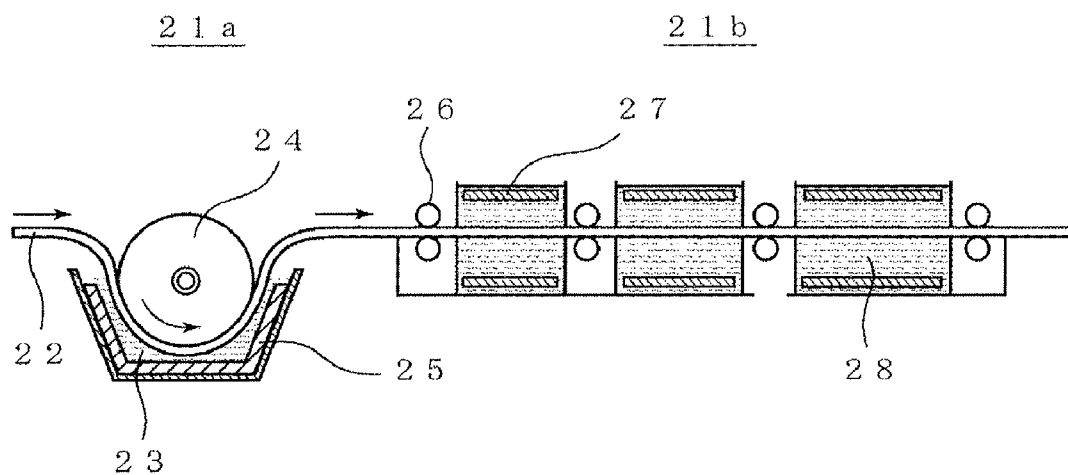
**FIG. 3**



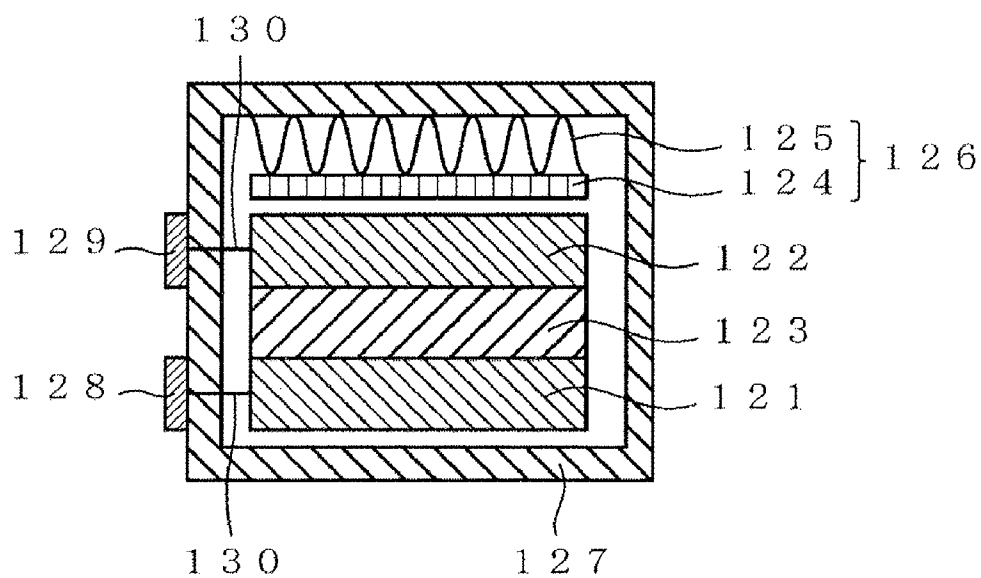
**FIG. 4**



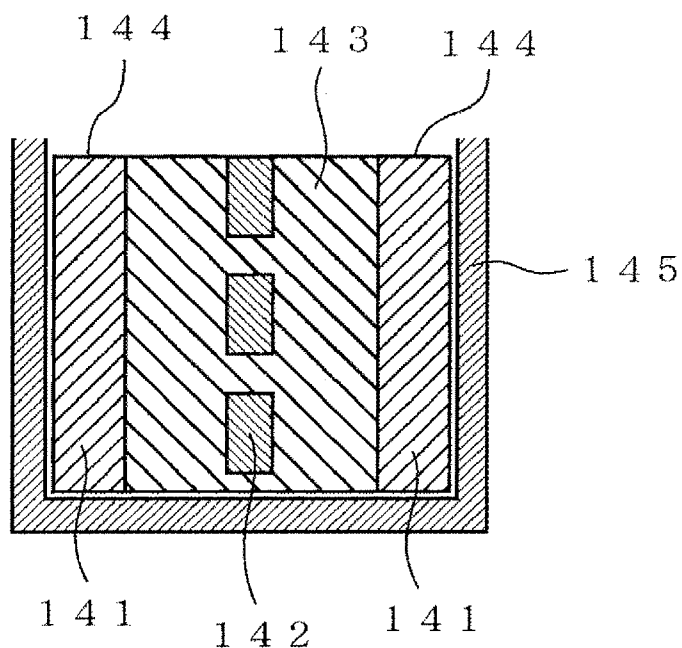
**FIG. 5**



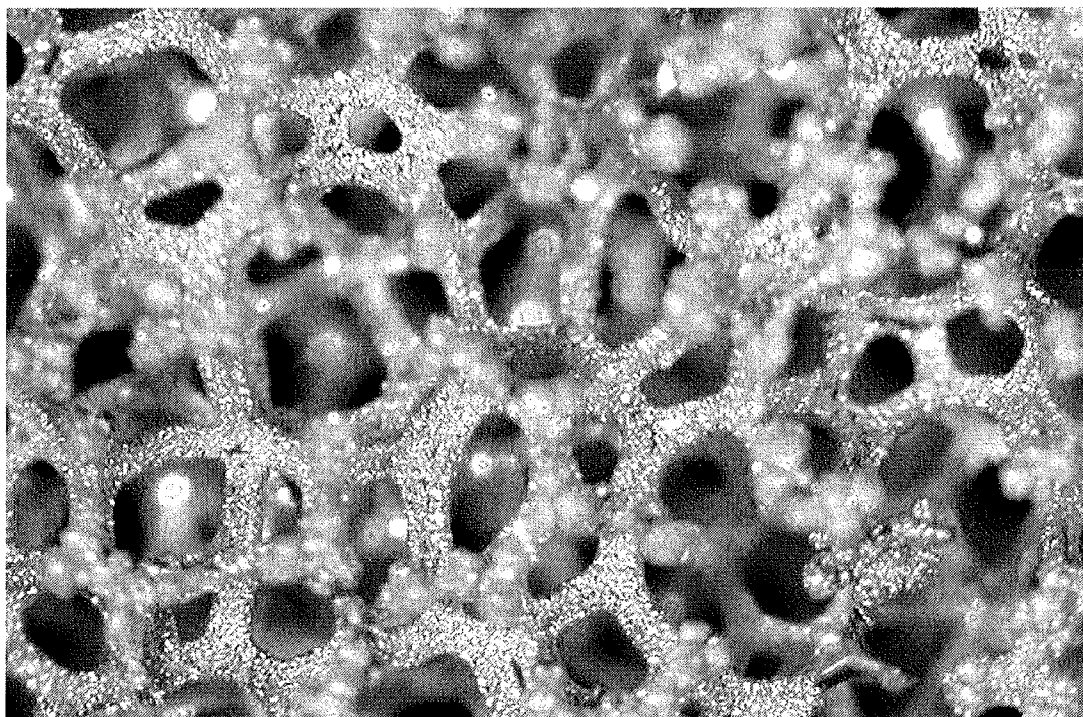
**FIG. 6**



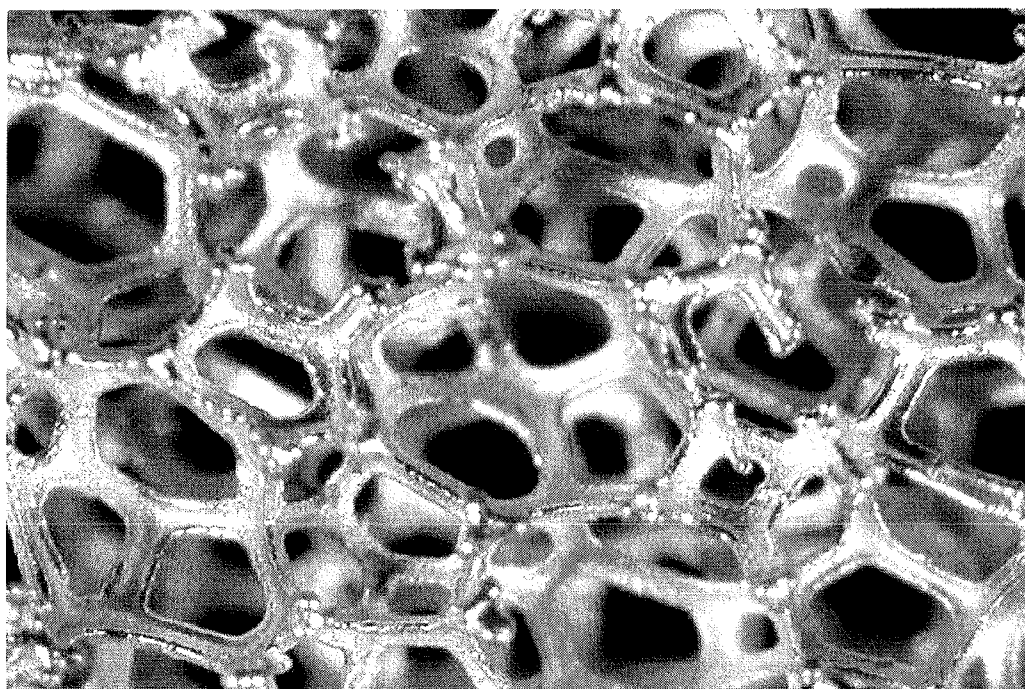
**FIG. 7**



**FIG. 8**



**FIG. 9**



## METHOD OF PRODUCING ALUMINUM STRUCTURE AND ALUMINUM STRUCTURE

### CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation application of International Application No. PCT/JP2012/050130 filed on Jan. 6, 2012 which claims priority on Japanese Patent Application No. 2011-002760 filed on Jan. 11, 2011, all of which are herein incorporated by reference.

### TECHNICAL FIELD

[0002] The present invention relates to a method for producing an aluminum structure on a resin surface by aluminum plating and, in particular, to an aluminum structure suitable for use as a metal porous body used in various filters, battery electrodes, etc., and a method for producing the aluminum structure.

### BACKGROUND ART

[0003] Metal porous bodies having a three-dimensional network structure are used in many fields including various filters, catalyst supports, and battery electrodes. For example, Celmet (registered trademark, product of Sumitomo Electric Industries, Ltd.) composed of nickel is used as an electrode material of batteries such as nickel-hydrogen batteries and nickel-cadmium batteries. Celmet is a metal porous body having continuous pores and characteristically has high porosity (90% or higher) compared to other porous bodies such as metal nonwoven fabrics. Celmet is obtained by forming a nickel layer on a surface of a skeleton of a porous resin, such as urethane foam, having continuous pores, performing a heat-treatment to decompose the foamed resin body, and then subjecting nickel to a reduction treatment. The nickel layer is formed by applying carbon powder or the like to a surface of a skeleton of the foamed resin body to make the body electrically conductive and then depositing nickel by electroplating.

[0004] Aluminum has outstanding characteristics such as electrical conductivity, corrosion resistance, and lightweightness. For use in batteries, for example, an aluminum foil having a surface coated with an active material such as lithium cobaltate is used as a positive electrode of a lithium ion battery. One conceivable approach to improving the capacity of a positive electrode is to make aluminum porous in order to increase the surface area and fill the interior of aluminum with an active material. This allows use of the active material even in a thick electrode and improves the ratio of making use of the active material per unit area. PTL 1 describes a method for forming a 2 to 20  $\mu\text{m}$  metallic aluminum layer on a plastic base having inner continuous spaces and a three-dimensional network shape by performing an aluminum vapor deposition process through an arc ion plating method. PTL 2 describes a method for obtaining a metal porous body by forming a coating film of a metal (copper or the like), which will form a eutectic alloy at a temperature equal to or lower than the melting point of aluminum, on a skeleton of a foamed resin body having a three-dimensional network structure, then applying an aluminum paste thereto, and conducting a heat treatment at a temperature of 550° C. or higher and 750° C. or lower in a non-oxidizing atmosphere to eliminate organic components (foamed resin) and sinter aluminum powder.

[0005] It is difficult to perform aluminum electroplating in aqueous-solution-based plating baths since aluminum has high affinity to oxygen and an electric potential lower than that of hydrogen. Due to this reason, non-aqueous-solution-based plating baths have been studied for aluminum electroplating. For example, PTL 3 discloses a technique of electroplating metal surfaces with aluminum to prevent oxidation, characterized in that a low-melting-point composition prepared by mixing and melting an onium halide and an aluminum halide is used as a plating bath and aluminum is deposited on a cathode while maintaining the water content in the bath at 2 wt % or less.

### CITATION LIST

#### Patent Literature

- [0006] [PTL 1] Japanese Patent No. 3413662  
[0007] [PTL 2] Japanese Unexamined Patent Application Publication No. 8-170126  
[0008] [PTL 3] Japanese Patent No. 3202072

### SUMMARY OF INVENTION

#### Technical Problem

[0009] Although PTL 1 describes that an aluminum porous body having a thickness of 2 to 20  $\mu\text{m}$  is obtained by the method disclosed therein, it is difficult to form a body having a large area since a gas phase method is used and it is difficult to form a layer that is uniform to the interior of the base depending on the thickness and the porosity of the base. There are also problems such as that formation of the aluminum layer is slow and the production cost is high due to high equipment costs. Moreover, when a thick film is formed, there is a risk that cracking may occur in the film and aluminum may come off. According to the method of PTL 2, a layer that forms a eutectic alloy with aluminum is formed and thus an aluminum layer having a high purity cannot be formed. Although aluminum electroplating methods are known, only metal surfaces can be plated by these methods and a method for electroplating a resin body surface, in particular, electroplating a porous resin body having a three-dimensional network structure, has not been known. This is presumably due to problems such as dissolution of the porous resin in plating baths.

[0010] Accordingly, an object of the present invention is to provide a method that enables formation of a high-purity aluminum structure, with which even a surface of a porous resin body having a three-dimensional network structure can be plated with aluminum and a thick film can be uniformly deposited, and a method with which a large-area aluminum porous body can be obtained.

#### Solution to Problem

[0011] In solving the problems described above, the inventors of the present application have conceived of a method for electroplating a surface of a resin body having a three-dimensional network structure such as polyurethane and melamine resins with aluminum. In other words, the present invention is a method for producing an aluminum structure, the method including plating a resin body having a three-dimensional network structure having at least a surface that has been made conductive with aluminum in a molten-salt bath, where the molten salt is a salt mixture of aluminum chloride and an

organic salt and plating is conducted while controlling the temperature of the molten-salt bath to be 45° C. or higher and 100° C. or lower.

**[0012]** The inventors have found that an aluminum plating method in which plating is conducted in a molten-salt bath which is a salt mixture of an organic salt and aluminum chloride is effective as a method for plating a surface of a resin body having a three-dimensional network structure with aluminum. Since a salt mixture of aluminum chloride and an organic salt such as an imidazolium salt is liquid at room temperature, the temperature of the plating bath is usually set to a temperature near room temperature. However, at a temperature near room temperature, the viscosity of the molten salt is high and satisfactory plating may not be formed on an article, such as a resin body having a three-dimensional network structure, having a complicated skeletal structure depending on the plating conditions. In particular, in order to form a large-area aluminum porous body, the current density needs to be increased; however, when the viscosity of the molten salt is low, the current density range in which plating is possible is narrowed. When the temperature of the molten-salt bath is adjusted to be 45° C. or higher and 100° C. or lower, the viscosity of the molten-salt bath can be decreased and the molten salt can be satisfactorily distributed throughout the interior of the resin body (porous body) having a three-dimensional network structure. Accordingly, uniform plating with a small difference in plating thickness between the surface portion and the inner portion of the porous body becomes possible. Moreover, since plating with a uniform thickness can be formed, the strength of the aluminum layer is increased and an aluminum structure with fewer breaks in the skeletal structure can be obtained after removal of the resin body.

**[0013]** The molten salt preferably further contains 1,10-phenanthroline in a concentration of 0.25 g/l or more and 7 g/l or less in order to improve the smoothness of the plating surface. When the temperature of the molten-salt bath is controlled within a particular range to decrease the viscosity and 1,10-phenanthroline is added, the skeleton surface is improved from a granular shape (surface has large irregularities and appears granular in surface observation) to a flat shape due to the synergetic effect of the two, and an aluminum structure that is strong and resistant to breaking can be obtained even with a thin skeleton having a small thickness.

**[0014]** The organic salt is preferably a molten salt containing nitrogen and an imidazolium salt is preferably used.

**[0015]** The molten salt bath is preferably a salt mixture of an imidazolium salt and aluminum chloride since the salt mixture melts at a relatively low temperature and has a high electrical conductivity. A salt containing an imidazolium cation having alkyl groups at 1,3-position is preferred as the imidazolium salt. In particular, a salt mixture of 1-ethyl-3-methylimidazolium chloride and aluminum chloride ( $\text{AlCl}_3$ -EMIC) is most preferable since it has high stability and is not readily decomposable. Since an imidazolium salt bath should not be used in the presence of water and oxygen, plating is preferably conducted in an inert gas atmosphere such as argon or nitrogen in a closed environment.

**[0016]** Urethane foam and melamine foam have high porosity, pore continuity, and favorable thermal decomposability and are thus preferably used as the resin porous body. Urethane foam is preferred from the viewpoints of pore uniformity and high availability and melamine foam is preferred since it has small pore diameter.

**[0017]** The technique for making the resin porous body surface electrically conductive can be selected from known methods. Metal layers of aluminum, nickel, etc., can be formed by electroless plating or a gas phase method and metal or carbon layers can be formed by using electrical conductive coating materials. Forming an aluminum layer by a gas phase method and imparting electrical conductivity by using carbon can be performed without adding metals other than aluminum to the aluminum structure after plating. Thus, a structure substantially composed of only aluminum as a metal can be produced.

**[0018]** An aluminum structure that includes a resin body having a metal layer on a surface is obtained through the aforementioned steps. The aluminum structure as is may be used as a resin-metal composite depending on the usage examples of which include various filters and catalyst supports. When limitations imposed by the operation environment require a resin-free metal structure, the resin may be removed.

**[0019]** Because of the two features described above, namely, resistance to breaking and a uniform plating thickness between the inside and outside, a uniformly pressed porous body having an entire skeleton resistant to breaking can be obtained by pressing the finished aluminum porous body. When an aluminum porous body is to be used as an electrode material of a battery or the like, an electrode is filled with an electrode active material and the density is increased by pressing. Since the skeleton tends to break during the active material filling step or during pressing, the aluminum structure is particularly effective in such a usage.

#### Advantageous Effects of Invention

**[0020]** According to the present invention, a surface of a porous resin body having a three-dimensional network structure can be plated with aluminum. Thus, a method that can form a large-area aluminum structure having a substantially uniform film thickness and high purity, and an aluminum structure can be provided.

#### BRIEF DESCRIPTION OF DRAWINGS

**[0021]** FIG. 1 is a flowchart showing steps for producing an aluminum structure according to the present invention.

**[0022]** FIG. 2 includes schematic cross-sectional views illustrating steps for producing an aluminum structure according to the present invention.

**[0023]** FIG. 3 is an enlarged photograph of a surface showing the structure of a urethane resin foam, which is an example of a porous resin body.

**[0024]** FIG. 4 is a diagram showing an example of a continuous process of imparting electrical conductivity to a resin body surface by using a conductive coating material.

**[0025]** FIG. 5 is a diagram showing an example of an aluminum continuous plating process that uses a molten salt plating.

**[0026]** FIG. 6 is a schematic cross-sectional view showing a structure example in which an aluminum porous body was adopted to a molten-salt battery.

**[0027]** FIG. 7 is a schematic cross-sectional view showing a structure example in which an aluminum porous body was adopted to an electrical double layer capacitor.

**[0028]** FIG. 8 is an enlarged photograph of a surface of an aluminum structure according to Example.

[0029] FIG. 9 is an enlarged photograph of a surface of an aluminum structure according to Example.

#### DESCRIPTION OF EMBODIMENTS

[0030] Embodiments of the present invention are described below with reference to drawings through a representative example of a process of producing an aluminum porous body. In the drawings referred to below, parts that are denoted by the same numeral are the same or corresponding parts. Note that the present invention is not limited by the embodiments but defined by the claims, and is intended to include all modifications and alterations within the meaning and scope of equivalents of the claims.

##### (Process of Producing Aluminum Structure)

[0031] FIG. 1 is a flowchart showing a process of producing an aluminum structure according to the present invention. FIG. 2 schematically illustrates how an aluminum structure is formed through the flowchart with a resin porous body as a core material. The flow of the overall production process will now be described by referring to these figures. First, a base resin body preparation 101 is performed. FIG. 2(a) is an enlarged schematic view showing an enlarged surface of a resin porous body (foamed resin body) having a three-dimensional network structure as an example of a base resin body. Pores are formed by a foamed resin body 1 serving as a skeleton. Next, imparting electrical conductivity to the resin body surface 102 is performed. In this step, as shown in FIG. 2(b), a conductive layer 2 composed of a thin conductor is formed on the surface of the foamed resin body 1. Then aluminum plating 103 is performed in a molten salt to form an aluminum plating layer 3 on the surface of the resin body on which the conductive layer is formed (FIG. 2(c)). As a result, an aluminum structure in which the aluminum plating layer 3 is formed on the surface of the resin body serving as a base is obtained. Additionally, base resin body removal 104 may be performed. An aluminum structure (porous body) constituted by only the metal layer remaining after removal of the foamed resin body 1 through decomposition or the like can be obtained (FIG. 2(d)). These steps are described below in sequence.

##### (Preparation of Resin Porous Body)

[0032] A resin porous body having a three-dimensional network structure is prepared. Any resin may be freely selected as the raw material of the resin porous body. Examples of the raw material include foamed resin bodies of polyurethane, melamine resins, polypropylene, polyethylene, etc. A resin porous body having any desired shape may be selected as long as pores that are continuous (continuous pores) are included. For example, a material having the shape of a nonwoven fabric in which resin fibers are entangled with one another can be used as a resin porous body. The porosity of the resin porous body is preferably 80% to 98% and the pore diameter is preferably 50 μm to 500 μm. The resin porous body is preferably formed of urethane foam or melamine foam since urethane foam and melamine foam have high porosity, pore continuity, and superior thermal decomposability. Urethane foam (urethane foam body) is preferred from the viewpoints of uniformity of pores and high availability and melamine foam is preferred from the viewpoint of small pore diameter.

[0033] A resin porous body often contains residual substances from a foam production process, such as foaming agents and unreacted monomers and thus a washing treatment is preferably performed for the subsequent steps. FIG. 3 shows an example of a resin porous body which has been subjected to a washing treatment as a pretreatment of urethane foam. The resin body serving as a skeleton constitutes a three-dimensional network and thus defines continuous pores throughout the entirety thereof. The urethane foam skeleton has a substantially triangular shape in a cross-section perpendicular to the direction in which the skeleton extends. The porosity is defined by the following equation:

$$\text{Porosity} = (1 - (\text{weight of porous material}[\text{g}] / (\text{volume of porous material}[\text{cm}^3] \times \text{density of raw material}))) \times 100 [\%]$$

[0034] The pore diameter is determined by enlarging a microscope image or the like of a resin body surface, counting the number of pores per inch (25.4 mm) to determine the cell number, and calculating an average value as mean pore diameter = 25.4 mm/cell number.

##### (Imparting Electrical Conductivity to Resin Porous Body Surface: Carbon Coating)

[0035] A carbon coating material is prepared as a conductive coating material. A suspension serving as a conductive coating material preferably contains carbon particles, a binder, a dispersant, and a dispersion medium. In order to uniformly form a coating of conductive particles, the suspension must maintain a homogeneous suspension state. Accordingly, the suspension is preferably maintained at 20° C. to 40° C. The reason for this is that when the temperature of the suspension is less than 20° C., a homogeneous suspension state is no longer maintained and only the binder is found in high concentration on a surface of the network-structured skeleton surface of the resin porous body and forms a layer. In such a case, the coating layer of carbon particles is easily separable and it is difficult to form a tightly adhering metal plating. In contrast, when the temperature of the suspension exceeds 40° C., the amount of the dispersant evaporating is large and the suspension becomes thicker with passage of the coating treatment time, and thereby fluctuations in the coating amount are likely to occur. The diameter of carbon particles is 0.01 to 5 μm and preferably 0.01 to 0.5 μm. When the particle diameter is large, the pores in the resin porous body may clog or smooth and flat plating is inhibited. When the particle diameter is excessively small, it is difficult to ensure sufficient electrical conductivity.

[0036] The resin porous body can be coated with carbon particles by immersing a subject resin porous body in the suspension and squeezing and drying the resin porous body. FIG. 4 is a diagram that schematically shows an example of an actual production process, which is a structural example of a processing system that imparts conductivity to a strip-shaped resin porous body serving as a skeleton. As shown in the drawing, this system includes a supply bobbin 12 that supplies a strip-shaped resin 11, a vessel 15 that contains a suspension 14 of a conductive coating material, a pair of squeezing rolls 17 arranged above the vessel 15, a plurality of hot air nozzles 16 arranged to face each other in the latter part of the travelling strip-shaped resin 11, and a take-up bobbin 18 that takes up the treated strip-shaped resin 11. Deflector rolls 13 for guiding the strip-shaped resin 11 are provided in appropriate places. In a system configured as such, the strip-

shaped resin **1** having a three-dimensional network structure is unwound from the supply bobbin **12**, guided via the deflector rolls **13**, and immersed in the suspension in the vessel **15**. The strip-shaped resin **11** immersed in the suspension **14** in the vessel **15** is turned upward and travels between the squeezing rolls **17** above the liquid surface of the suspension **14**. At this time, the gap between the squeezing rolls **17** is smaller than the thickness of the strip-shaped resin **11** and the strip-shaped resin **11** is compressed. Accordingly, excess suspension in the strip-shaped resin **11** is squeezed out and returns to the vessel **15**.

**[0037]** Next, the direction in which the strip-shaped resin **11** travels is changed again. Hot air blown from the hot air nozzles **16** constituted by a plurality of nozzles, removes the dispersion medium and the like of the suspension and the strip-shaped resin **11** thoroughly dried is taken up by the take-up bobbin **18**. The temperature of hot air blown from the hot air nozzles **16** is preferably in a range of 40° C. to 80° C. When such a system is used, a conductivity-imparting process can be performed automatically and continuously and a skeleton that has a network structure free of clogging and a uniform conductive layer is formed. Thus, the subsequent step, i.e., metal plating, can be smoothly carried out.

#### (Formation of Aluminum Layer: Molten Salt Plating)

**[0038]** Next, electrolytic plating is performed in a molten salt to form an aluminum plating layer on a resin porous body surface. A DC current is applied to the resin porous body having a conductive surface as a cathode and an aluminum plate having a purity of 99.99% as an anode in the molten salt. A mixed salt (eutectic salt) containing aluminum chloride and an organic salt is used as the molten salt. An organic molten-salt bath that melts at a relatively low temperature is preferably used since plating can be conducted without decomposition of the resin porous body serving as a base. An imidazolium salt, a pyridinium salt, or the like can be used as the organic salt. In particular, 1-ethyl-3-methylimidazolium chloride (EMIC) and butylpyridinium chloride (BPC) are preferred.

**[0039]** The temperature of the molten-salt bath is adjusted to be 45° C. or higher and 100° C. or lower to decrease the viscosity of the molten salt. When the temperature is less than 45° C., the viscosity cannot be sufficiently decreased. When the temperature is more than 100° C., the organic salt may decompose. A more preferable temperature is 50° C. or more and 80° C. or less. Mixing of water or oxygen into the molten salt deteriorates the molten salt. Thus, plating is preferably conducted in an inert gas atmosphere such as nitrogen, argon, or the like, in a closed environment.

**[0040]** To the molten-salt bath, 1,10-phenanthroline is preferably added to make the surface smooth. The amount of 1,10-phenanthroline added is preferably 0.25 g/l or more and 7 g/l or less. When the amount added is less than 0.25 g/l, the effect of making the surface smooth is not easily obtained. The effect of making the surface smooth is enhanced as the amount of 1,10-phenanthroline added increases; however, the effect does not improve much at an amount larger than 7 g/l. A more preferable range of the amount added is 2.5 g/l or more and 5 g/l or less.

**[0041]** According to a method of decreasing the viscosity by adding an organic solvent or the like to the molten-salt bath, equipment for preventing evaporation of the organic solvent and safety equipment for preventing ignition of the organic solvent are necessary; however, according to the

present invention, the viscosity of the molten-salt bath is decreased by controlling the temperature within a particular range. Thus, plating can be performed with simple equipment. Moreover, the effects are the same since 1,10-phenanthroline does not evaporate in a range of 45° C. to 100° C.

**[0042]** FIG. 5 is a diagram schematically showing a structure of a system for continuously conducting a metal plating treatment on the strip-shaped resin described above. In the structure shown in the drawing, a strip-shaped resin **22** having a conductive surface is transported from left to right. A first plating vessel **21a** is constituted by a cylindrical electrode **24**, an anode **25** installed to the inner wall of the container, and a plating bath **23**. The strip-shaped resin **22** passes through the plating bath **23** along the cylindrical electrode **24** so that electrical currents can easily and evenly flow in the entire resin porous body and a uniform plating can be formed. A second plating vessel **21b** is a vessel for forming thick and uniform plating and is constituted by a plurality of vessels so that plating is repeatedly performed. Plating is conducted by sequentially sending the strip-shaped resin **22** having a conductive surface through a plating bath **28** by using transfer rollers and electrode rollers **26** serving as out-of-vessel power-feed cathodes. Anodes **27** are disposed in the plurality of vessels so as to face the two sides of the resin porous body with the plating bath **28** therebetween. Both sides of the resin porous body can be plated more uniformly.

**[0043]** An aluminum structure (aluminum porous body) having a resin porous body as the core of the skeleton is obtained through the aforementioned steps. The aluminum structure as is may be used as a resin-metal composite depending on the usage examples of which include various filters and catalyst supports. When limitations imposed by the operation environment require a resin-free metal structure, the resin may be removed. The resin may be removed by any desired method such as decomposition (dissolution) using an organic solvent, a molten salt, or a supercritical water, or pyrolysis. Unlike nickel and the like, aluminum is difficult to reduce once it is oxidized. Thus, when aluminum is used as an electrode material of a battery etc., the resin is preferably removed by a method that does not readily cause oxidation of aluminum. For example, a method of removing the resin by pyrolysis in a molten salt described below is preferably used.

#### (Removal of Resin: Pyrolysis in Molten Salt)

**[0044]** Pyrolysis in a molten salt is conducted by the following method. A resin porous body having an aluminum plating layer formed on a surface is immersed in a molten salt and the resin porous body is decomposed under heating by applying a negative potential to the aluminum layer. When a negative potential is applied while the body is immersed in a molten salt, the resin porous body can be decomposed without oxidation of aluminum. The heating temperature can be selected according to the type of the resin porous body but the process must be conducted at a temperature equal to or less than the melting point of aluminum (660° C.) in order not to melt aluminum. A preferable temperature range is 500° C. or more and 600° C. or less. The amount of the negative potential applied is to be lower than the reduction potential of aluminum but higher than the reduction potential of a cation in a molten salt.

**[0045]** A halide salt or nitrate of an alkali metal or an alkaline earth metal that renders the electrode potential of aluminum to be less noble can be used as a molten salt used for pyrolysis of the resin. In particular, the molten salt pref-

erably contains at least one selected from the group consisting of lithium chloride ( $\text{LiCl}$ ), potassium chloride ( $\text{KCl}$ ), sodium chloride ( $\text{NaCl}$ ), aluminum chloride ( $\text{AlCl}_3$ ), lithium nitrate ( $\text{LiNO}_3$ ), lithium nitrite ( $\text{LiNO}_2$ ), potassium nitrate ( $\text{KNO}_3$ ), potassium nitrite ( $\text{KNO}_2$ ), sodium nitrate ( $\text{NaNO}_3$ ), and sodium nitrite ( $\text{NaNO}_2$ ). According to this method, an aluminum porous body having a thin oxide layer on the surface and a low oxygen content can be obtained.

#### (Lithium Ion Battery)

**[0046]** Next, a battery electrode material and a battery that use an aluminum porous body are described. For example, when an aluminum porous body is used in a positive electrode of a lithium ion battery, lithium cobalt oxide ( $\text{LiCoO}_2$ ), lithium manganate ( $\text{LiMn}_2\text{O}_4$ ), lithium nickelate ( $\text{LiNiO}_2$ ), or the like is used as an active material. The active material is used in combination with a conductive aid and a binder. In a known positive electrode material for a lithium ion battery, a surface of an aluminum foil is coated with the active material. The thickness of the active material coating is increased to improve the battery capacity per unit area. In order to effectively use the active material, the aluminum foil and the active material need to make an electrical contact and thus the active material is mixed with a conductive aid. In contrast, the aluminum porous body of the present invention has a high porosity and a large surface area per unit area. Accordingly, the active material can be effectively used even when a thin active material is supported on the surface of the porous body, the capacity of the battery can be improved, and the amount of the conductive aid to be mixed can be reduced. A lithium ion battery uses the positive electrode material described above as the positive electrode, graphite as the negative electrode, and an organic electrolyte solution as an electrolyte. Since such a lithium ion battery can have an improved capacity despite a small electrode area, the energy density of the battery can be increased compared to known lithium ion batteries.

#### (Molten-Salt Battery)

**[0047]** An aluminum porous body can also be used as an electrode material for a molten-salt battery. When an aluminum porous body is used as a positive electrode material, a metal compound that can intercalate a cation of a molten salt serving as an electrolyte, e.g., sodium chromite ( $\text{NaCrO}_2$ ) or titanium disulfide ( $\text{TiS}_2$ ), is used as the active material. The active material is used in combination with a conductive aid and a binder. Acetylene black and the like can be used as the conductive aid. Polytetrafluoroethylene (PTFE) and the like can be used as the binder. When sodium chromite is used as the active material and acetylene black is used as the conductive aid, PTFE is preferred since it can firmly bond the two together.

**[0048]** The aluminum porous body can also be used as a negative electrode material of a molten salt battery. When an aluminum porous body is used as the negative electrode material, elemental sodium, an alloy of sodium and other metals, carbon, etc., can be used as the active material. Since the melting point of sodium is about  $98^\circ\text{C}$ . and the metal softens with an increase in temperature, sodium is preferably alloyed with another metal (Si, Sn, In, or the like). In particular, an alloy of sodium and Sn is preferred since the alloy is easy to handle. Sodium or a sodium alloy can be supported on the surface of the aluminum porous body by electrolytic plating,

hot-dipping, or the like. Alternatively, a sodium alloy can be formed by depositing a metal to be alloyed with sodium onto an aluminum porous body by plating or the like and then conducting charging in the molten-salt battery.

**[0049]** FIG. 6 is a schematic cross-sectional view showing an example of a molten-salt battery that uses the battery electrode material described above. The molten-salt battery includes a positive electrode **121** in which a positive electrode active material is supported on the surface of the aluminum skeleton portion of an aluminum porous body, a negative electrode **122** in which a negative electrode active material is supported on the surface of the aluminum skeleton portion of an aluminum porous body, and a separator **123** impregnated with a molten salt serving as an electrolyte. The positive electrode **121**, the negative electrode **122**, and the separator **123** are housed in a case **127**. A presser member **126** constituted by a presser plate **124** and a spring **125** that presses the presser plate is disposed between the upper surface of the case **127** and the negative electrode. Because the presser member is provided, all components can be pressed uniformly and brought into contact with each other even when the positive electrode **121**, the negative electrode **122**, and the separator **123** undergo volume changes. A collector (aluminum porous body) for the positive electrode **121** and a collector (aluminum porous body) for the negative electrode **122** are respectively connected to a positive electrode terminal **128** and a negative electrode terminal **129** via lead wires **130**.

**[0050]** Various inorganic salts or organic salts that melt at an operating temperature can be used as the molten salt that serves as an electrolyte. At least one selected from alkali metals such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs) and alkaline earth metals such as beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), and barium (Ba), can be used as the cation of the molten salt.

**[0051]** In order to decrease the melting point of the molten salt, two or more salts are preferably used as a mixture. For example, when potassium bis(fluorosulfonyl)amide (KFSA) and sodium bis(fluorosulfonyl)amide (NaFSA) are used in combination, the operating temperature of the battery can be controlled to be  $90^\circ\text{C}$ . or less.

**[0052]** The molten salt is used by impregnating the separator. The separator is provided to prevent the positive electrode and the negative electrode from contacting each other and a glass nonwoven fabric, a porous resin porous body, etc., can be used as the separator. The positive electrode, the negative electrode, and the separator impregnated with the molten salt are stacked, housed in the case, and used as a battery.

#### (Electrical Double Layer Capacitor)

**[0053]** An aluminum porous body can also be used as an electrode material for an electrical double layer capacitor. When an aluminum porous body is used as an electrode material for an electrical double layer capacitor, activated carbon or the like is used as an electrode active material. Activated carbon is used in combination with a conductive aid and a binder. Graphite, carbon nanotube, and the like can be used as the conductive aid. Polytetrafluoroethylene (PTFE), styrene butadiene rubber, etc., can be used as the binder.

**[0054]** FIG. 7 is a schematic cross-sectional view showing one example of an electrical double layer capacitor that uses the electrode material for an electrical double layer capacitor described above. An electrode material in which an electrode active material is supported on an aluminum porous body is

disposed in an organic electrolyte solution **143** partitioned with a separator **142**, and functions as a polarizable electrode **141**. The electrode material **141** is connected to a lead wire **144** and all of these components are housed in a case **145**. Because the aluminum porous body is used as a collector, the surface area of the collector is increased and an electrical double layer capacitor that has high output and high capacity can be obtained even when activated carbon serving as an active material is applied thinly.

(Formation of Conductive Layer: Carbon Coating)

**[0055]** A production example of an aluminum porous body is specifically described below. A urethane foam having a thickness of 1 mm, a porosity of 95%, and a pore diameter of 300  $\mu\text{m}$  was prepared as a resin porous body and cut into a 80 mm $\times$ 50 mm piece. The urethane foam was immersed in a carbon suspension and dried to cause carbon particles to adhere to the entire surface and thereby form a conductive layer. The suspension contained 25% of graphite+carbon black, a resin binder, a penetrant, and an antifoamer. The particle diameter of the carbon black was 0.5  $\mu\text{m}$ .

(Formation of Conductive Layer: Aluminum Vapor Deposition)

**[0056]** The same resin porous body used in carbon coating was prepared and aluminum was vapor-deposited on the surface to form an aluminum conductive layer having a thickness of 0.7  $\mu\text{m}$ .

(Molten Salt Plating)

**[0057]** A urethane foam having a conductive layer on the surface was used as a work. The work was set to a fixture having a power-supplying function, placed in an argon-atmosphere glove box having a low moisture content (dew point:  $-30^{\circ}\text{C}$ . or less), and immersed in a molten bath (33 mol % EMIC-67 mol %  $\text{AlCl}_3$ ) at a temperature shown in Tables 1 and 2. Note that 1,10-phenanthroline in a concentration shown in Tables 1 and 2 was added to the molten-salt bath. The fixture to which the work was set was connected to the cathode side of a rectifier and an aluminum plate (purity: 99.99%) was connected to the counter electrode, anode. A DC

current having a current density shown in Table 1 was applied for 90 minutes in the case of 2 A/cm<sup>2</sup> (hereinafter, "A/cm<sup>2</sup>" is denoted as ASD), 30 minutes in the case of 6 ASD, and 10 minutes in the case of 15 ASD to form aluminum plating. Stirring was conducted with a stirrer using a Teflon (registered trademark) rotor. The current density is a value calculated based on the apparent area of the urethane foam.

(Decomposition of Resin Porous Body)

**[0058]** Each resin porous body on which an aluminum plating layer was formed was immersed in a LiCl—KCl eutectic molten salt having a temperature of 500° C., and a negative potential of -1 V was applied for 5 minutes to decompose and remove polyurethane and to thereby obtain an aluminum porous body.

**[0059]** The platability in the interior of the obtained aluminum porous body was evaluated. Regarding evaluation of the plating inside, samples in which the thickness of the plating on the interior of the porous body was small and the plating separated into two pieces after removal of the urethane foam were rated F and samples in which the interior of the porous body was plated and separation did not occur were rated A. Regarding the evaluation of a cross section, from the samples in which the interior of the porous body was plated and the separation did not occur, a surface portion and a cross-section taken at a section perpendicular to the direction in which the skeleton extends were extracted, embedded in a resin, and polished to observe the cross sections. In observation of the cross-section, samples in which the thickness of the plating inside was 70% or more of the thickness of the plating outside were rated A, samples in which the thickness of the plating inside was 50% or more and less than 70% of the thickness of the plating outside were rated B, and samples in which the thickness of the plating inside was less than 50% of the thickness of the plating outside were rated F. In order to evaluate the surface smoothness of the plating (this is indicated as "Surface" in the tables), the aluminum porous body was observed with a scanning electron microscope. Samples having a smooth surface at  $\times 1000$  magnification were rated A and Samples with clear and large irregularities were rated F. The results are shown in Tables 1 and 2.

TABLE 1

| (Results from samples in which an aluminum conductive layer was formed) |                   |                                    |                  |                  |                  |                  |
|-------------------------------------------------------------------------|-------------------|------------------------------------|------------------|------------------|------------------|------------------|
|                                                                         |                   | Phenanthroline concentration (g/l) |                  |                  |                  |                  |
|                                                                         |                   |                                    | 0.25             |                  | 2.5              | 5                |
| Temperature                                                             | (Current density) | 2 ASD                              | 6 ASD            | 15 ASD           | 6 ASD            | 6 ASD            |
|                                                                         |                   | Plating                            | Plating          | Plating          | Plating          | Plating          |
|                                                                         |                   | inside: F                          | inside: F        | inside: F        | inside: F        | inside: F        |
|                                                                         |                   | Surface: A                         | Surface: F       | Surface: F       | Surface: A       | Surface: A       |
|                                                                         |                   | Cross-section: F                   | Cross-section: F | Cross-section: F | Cross-section: F | Cross-section: F |
|                                                                         | Room temperature  | 2 ASD                              | 6 ASD            | 15 ASD           | 6 ASD            | 6 ASD            |
|                                                                         |                   | Plating                            | Plating          | Plating          | Plating          | Plating          |
|                                                                         |                   | inside: A                          | inside: A        | inside: A        | inside: A        | inside: A        |
|                                                                         |                   | Surface: A                         | Surface: F       | Surface: F       | Surface: A       | Surface: A       |
|                                                                         |                   | Cross-section: F                   | Cross-section: F | Cross-section: F | Cross-section: F | Cross-section: A |

TABLE 1-continued

| (Results from samples in which an aluminum conductive layer was formed) |                                                                 |                                                                 |                                                                  |                                                                 |
|-------------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|------------------------------------------------------------------|-----------------------------------------------------------------|
| Phenanthroline concentration (g/l)                                      |                                                                 |                                                                 |                                                                  |                                                                 |
|                                                                         | 0.25                                                            | 2.5                                                             | 5                                                                |                                                                 |
| (Current density)<br>80° C.                                             | 2 ASD<br>Plating<br>inside: A<br>Surface: A<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: F<br>Cross-section: F | 15 ASD<br>Plating<br>inside: A<br>Surface: F<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: A<br>Cross-section: B |

| (Results from samples in which a carbon conductive layer was formed) |                                                                 |                                                                 |                                                                 |                                                                 |
|----------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------|
| Phenanthroline concentration (g/l)                                   |                                                                 |                                                                 |                                                                 |                                                                 |
|                                                                      | 0.25                                                            | 1.25                                                            | 2.5                                                             | 5                                                               |
| Temperature (Current density)<br>Room temperature                    | 6 ASD<br>Plating<br>inside: F<br>Surface: F<br>Cross-section: F | 6 ASD<br>Plating<br>inside: F<br>Surface: A<br>Cross-section: F | 6 ASD<br>Plating<br>inside: F<br>Surface: A<br>Cross-section: F | 6 ASD<br>Plating<br>inside: F<br>Surface: A<br>Cross-section: F |
| (Current density)<br>60° C.                                          | 6 ASD<br>Plating<br>inside: A<br>Surface: F<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: F<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: A<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: A<br>Cross-section: A |
| (Current density)<br>80° C.                                          | 6 ASD<br>Plating<br>inside: A<br>Surface: F<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: F<br>Cross-section: F | 6 ASD<br>Plating<br>inside: A<br>Surface: A<br>Cross-section: B | 6 ASD<br>Plating<br>inside: A<br>Surface: A<br>Cross-section: B |

**[0060]** As shown in Tables 1 and 2, the platability inside was poor when the plating temperature was room temperature and the plating separated into two pieces after removal of the urethane foam. Separation did not occur when the plating temperature was 60° C. or 80° C. and the interior was platable. However, cross-section evaluation and surface evaluation in which the state of plating was closely observed, many samples rated F were found when the phenanthroline concentration was 0.25 g/l. In particular, the evaluation results worsened as the current density was increased. When the amount of phenanthroline added is small, the current density needs to be low and plating needs to be slowly conducted in order to improve the surface smoothness of the plating.

**[0061]** FIG. 8 is a scanning electron microscope photograph of an aluminum structure prepared by plating a sample having an aluminum conductive layer with aluminum at a phenanthroline concentration of 0.25 g/l, a current density of 6 ASD, and a plating temperature of 60° C. FIG. 9 is a scanning electron microscope photograph of an aluminum structure prepared by plating a sample having an aluminum conductive layer with aluminum at a phenanthroline concentration of 5 g/l, a current density of 6 ASD, and a plating temperature of 60° C. It can be understood that the surface of the aluminum plating is smooth in FIG. 9 in which the

phenanthroline concentration is high but irregularities are formed on the surface in FIG. 8 in which the phenanthroline concentration is low.

#### INDUSTRIAL APPLICABILITY

**[0062]** As discussed above, according to the present invention, a structure prepared by plating a resin body surface with aluminum and an aluminum structure prepared by removing the resin body from this structure can be obtained. Thus, for example, the present invention can be adopted to an aluminum porous body and can be used in a wide variety of fields in which characteristics of aluminum are fully utilized, such as in electric materials such as battery electrodes, filters for filtration, and catalyst supports.

#### REFERENCE SIGNS LIST

- [0063]** 1 foamed resin body
- [0064]** 2 conductive layer
- [0065]** 3 aluminum plating layer
- [0066]** 11 strip-shaped resin
- [0067]** 12 supply bobbin
- [0068]** 13 deflector roll
- [0069]** 14 suspension
- [0070]** 15 vessel
- [0071]** 16 hot air nozzle
- [0072]** 17 squeezing roll
- [0073]** 18 take-up bobbin
- [0074]** 21a, 21b plating vessel
- [0075]** 22 strip-shaped resin
- [0076]** 23, 28 plating bath
- [0077]** 24 cylindrical electrode
- [0078]** 25, 27 positive electrode
- [0079]** 26 electrode roller
- [0080]** 121 positive electrode
- [0081]** 122 negative electrode
- [0082]** 123 separator
- [0083]** 124 presser plate
- [0084]** 125 spring
- [0085]** 126 presser member
- [0086]** 127 case
- [0087]** 128 positive electrode terminal
- [0088]** 129 negative electrode terminal
- [0089]** 130 lead wire
- [0090]** 141 polarizable electrode
- [0091]** 142 separator
- [0092]** 143 organic electrolyte solution
- [0093]** 144 lead wire
- [0094]** 145 case

1. A method for producing an aluminum structure, comprising a step of plating a resin porous body having a three-dimensional network structure with aluminum in a molten-salt bath, the resin porous body at least having a surface that has been made electrically conductive,

wherein the molten salt is a salt mixture of aluminum chloride and an organic salt and plating is performed by controlling the temperature of the molten-salt bath to be 45° C. or more and 100° C. or less.

2. The method for producing an aluminum structure according to claim 1, wherein the molten-salt bath further contains 1,10-phenanthroline at a concentration of 0.25 g/l or more and 7 g/l or less.

3. The method for producing an aluminum structure according to claim 1, wherein the organic salt is an imidazolium salt.

4. The method for producing an aluminum structure according to claim 1, wherein the resin porous body is polyurethane or melamine resin.

5. The method for producing an aluminum structure according to claim 1, further comprising a step of removing the resin porous body after the step of plating.

6. An aluminum structure produced by the method according to claim 1.

\* \* \* \* \*