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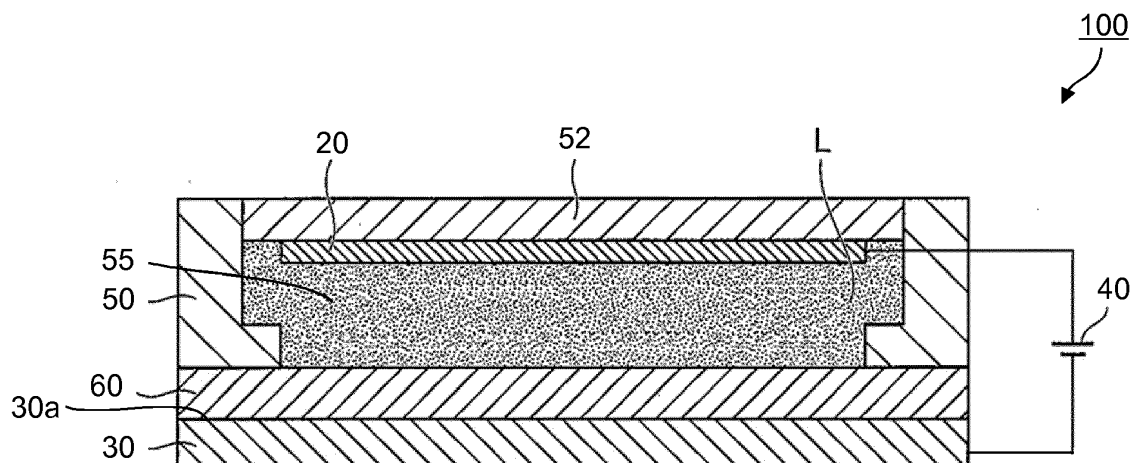
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(54) **FILM FORMING DEVICE AND METHOD FOR FORMING METAL FILM USING THE SAME**

(57) A film forming device 100 for forming a metal film at a high current efficiency and a method for forming the metal film using the film forming device 100 are provided. The film forming device 100 to form the metal film includes an anode 20, a cathode 30, a porous membrane 60 disposed between the anode 20 and the cathode 30 to be capable of contacting the cathode 30, a solution

container 50 defining a solution containing space 55 between the anode 20 and the porous membrane 60, and a power supply 40 applying a voltage between the anode 20 and the cathode 30. The porous membrane 60 is composed of a polyolefin chain without an ion-exchange functional group.

Fig. 1



Description

BACKGROUND

5 Technical Field

[0001] The present disclosure relates to a film forming device for forming a metal film and a method for forming the metal film using the same.

10 Background Art

[0002] Conventionally, there has been widely used a plating method as a method for forming a film of metal such as tin and nickel. However, the plating method has required a rinse with water after a plating treatment, and a processing of waste liquid. Therefore, JP 2016-169399 A describes a method referred to as a solid electrolyte deposition (SED) method as a method for forming a metal coating. In the solid electrolyte deposition method described in JP 2016-169399 A, a solid electrolyte membrane is disposed between an anode and a cathode (substrate), an aqueous solution containing metal ions is provided between the anode and the solid electrolyte membrane, the solid electrolyte membrane is brought into contact with the substrate, and a voltage is applied between the anode and the cathode, such that the metal ions turn into metal deposit on the substrate to form a metal coating on a surface of the substrate.

20 **[0003]** Further, JP 2015-218366 A teaches that a separator (separation membrane) modified by introducing a carboxylic acid group or its derivative is used as a separator for separating a cathode from an anode chamber in an electroplating cell.

SUMMARY

25 **[0004]** The solid electrolyte membrane described in JP 2016-169399 A and the separation membrane described in JP 2015-218366 A have ion-exchange functional groups. According to examinations by the inventor, the solid electrolyte deposition methods using such membranes have a problem of low current efficiency.

[0005] The present disclosure provides a film forming device capable of forming a metal film at a high current efficiency, in other words, at a high film forming rate and a method for forming the metal film using the film forming device.

30 **[0006]** According to a first aspect of the present disclosure, there is provided a film forming device for forming a metal film that includes an anode, a cathode, a porous membrane, a solution container, and a power supply. The porous membrane is disposed between the anode and the cathode to be capable of contacting the cathode. The solution container defines a solution containing space between the anode and the porous membrane. The power supply applies a voltage between the anode and the cathode. The porous membrane is composed of a polyolefin chain without an ion-exchange functional group.

35 **[0007]** According to a second aspect of the present disclosure, there is provided a method for forming a film of metal that includes applying a voltage between the anode and the cathode in the film forming device according to the first aspect in a state where the solution containing space is filled with a liquid electrolyte containing ions of the metal and the porous membrane is in contact with the cathode.

40 **[0008]** The porous membrane used in the film forming device of the present disclosure does not have the ion-exchange functional group and therefore metal ions are allowed to pass through the inside of the porous membrane without being trapped in the membrane. Accordingly, the metal film can be formed at a high current efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

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[0009]

FIG. 1 is a cross-sectional view schematically illustrating an example of a film forming device;

50 FIG. 2 is a flowchart for a metal film forming method; and

FIG. 3 is a graph depicting a relationship between a pore diameter and a current efficiency in nickel film formation.

DETAILED DESCRIPTION

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<Film Forming Device>

[0010] As illustrated in FIG. 1, a film forming device 100 according to an embodiment includes an anode 20, a cathode

30, a porous membrane 60, a solution container 50 defining a solution containing space 55, and a power supply 40 applying a voltage between the anode 20 and the cathode 30. The solution containing space 55 is a space to contain a liquid electrolyte L containing metal ions.

(1) Anode 20

[0011] The anode 20 is corrosion-resistant to the liquid electrolyte L containing the metal ions and has a conductivity that allows the anode 20 to function as an electrode. For example, the anode 20 may be formed of a metal (for example, gold) having a standard oxidation-reduction potential (standard electrode potential) higher than a standard oxidation-reduction potential of the metal in the liquid electrolyte L, or a metal same as the metal in the liquid electrolyte L. A shape and an area of the anode 20 may be appropriately designed according to a shape and an area of a metal film forming area on a surface of the cathode 30.

(2) Cathode 30

[0012] The cathode 30 is also corrosion-resistant to the liquid electrolyte L containing the metal ions and has a conductivity that allows the cathode 30 to function as an electrode. The metal film formed by the film forming device 100 is formed on the surface of the cathode 30. Therefore, a substrate to be coated with the metal film is usable as the cathode 30.

(3) Porous Membrane 60

[0013] The porous membrane 60 is disposed between the anode 20 and the cathode 30 such that the porous membrane 60 can contact the cathode 30. The porous membrane 60 may be movable between a position where the porous membrane 60 is separated from the cathode 30 and a position where the porous membrane 60 is in contact with the cathode 30.

[0014] The porous membrane 60 is composed of a polyolefin chain. The porous membrane 60 may be composed of, for example, polyethylene, polypropylene, or a mixture of these substances. The polyolefin refers to all olefin polymers. The polyolefin chain may be cross-linked or non-cross-linked, may be saturated or unsaturated, or may be straight-chained or branched. Although the polyolefin chain may be substituted or unsubstituted, the polyolefin chain is without an ion-exchange functional group. In some embodiments, the polyolefin chain can be exemplified by a cross-linked or non-cross-linked polyethylene chain without a side chain. The porous membrane 60 without the ion-exchange functional group can be disposed of without a special treatment after the use.

[0015] Here, the functional group is an atom or an atom group responsible for reactivity characteristic of an organic compound and also referred to as a functional atomic group or a functioning group. The ion exchange functional group includes both of a cation exchange functional group and an anion exchange functional group. The cation exchange functional group includes a sulfonic acid group, a sulfonimide group, a sulfone methide group, a phosphonic acid group, a carboxylic acid group, and the like. The anion exchange functional group includes a quaternary ammonium group, a quaternary pyridinium group, primary to tertiary amino groups, a pyridyl group, an imidazolyl group, and the like. A group other than the ion-exchange functional group (a non-ion-exchangeable group) includes an alkyl group, an olefin group, an acetylene group, and an aromatic group. "Without an ion-exchange functional group" means that the ion-exchange functional group is completely absent (that is, only a group other than the ion-exchange functional group is present) or present only in an amount not affecting the reactivity of the polyolefin chain. Specifically, the polyolefin chain without the ion-exchange functional group includes the polyolefin chain having the ion-exchange functional group in an amount such that a ratio of the number of oxygen atoms to that of carbon atoms in the porous membrane 60 obtained by X-ray photoelectron spectroscopy analysis method is 0.1 or less, or 0.02 or less in some embodiments.

[0016] The presence/absence of the ion-exchange functional group can be examined by various qualitative analysis methods and quantitative analysis methods. An appropriate qualitative analysis method may be selected depending on the functional group. For example, the presence/absence of the sulfonic acid group can be examined by an alkali fusion test, a ferric hydroxamate test, or the like. The presence/absence of the carboxylic acid group can be examined by ferric hydroxamate test, pH test, or the like. Examples of the quantitative analysis method include an ultraviolet spectroscopy method, an infrared spectroscopy method, a Raman spectroscopy method, a nuclear magnetic resonance spectroscopy method, a mass analysis method, an X-ray analysis, and the like.

[0017] The porous membrane 60 may have a pore diameter of 20 to 2000 nm, or 27 to 1000 nm in some embodiments. The pore diameter within the range allows forming the metal film at a high current efficiency. Here, the pore diameter means a volume mean diameter of a pore diameter distribution. The pore diameter distribution can be obtained by a mercury penetration method compliant with JIS R 1655: 2003. In the mercury penetration method, a pressure is applied to cause the mercury to enter open pores of the porous membrane, and a relationship between a volume of the mercury that has entered the open pores and a pressure value applied at the time is obtained, then, based on the obtained

relationship, diameters of the open pores are calculated using Washburn's equation assuming that the open pores have columnar shapes.

[0018] A solid electrolyte membrane used for the conventional solid electrolyte deposition method has flow passages formed therein, the flow passages having diameters of several nanometers respectively and referred to as ion channels. The ion channel is defined by a wall surface (surface) of the solid electrolyte membrane. On the wall surface of the solid electrolyte membrane, the ion-exchange functional group is present. When a voltage is applied between the anode and the cathode, metal ions move from the anode to the cathode via the ion channel. According to examinations by the inventor, since the ion channel has a small diameter and the ion-exchange functional group is present, the metal ions are easily trapped by the ion-exchange functional group by a Coulomb force. Therefore, transport efficiency of the metal ions inside the solid electrolyte membrane is low and the current efficiency is low as well. Meanwhile, the porous membrane 60 used in the film forming device 100 of the embodiment has the pore diameter larger than that of the solid electrolyte membrane. Accordingly, the metal ions are not trapped in the pores and can move the inside of the porous membrane 60 at a high efficiency and high speed, and consequently the film of the metal can be formed at a high current efficiency.

[0019] Air permeability of the porous membrane 60 may be 5 to 500 s/100 cm³, and 10 to 260 s/100 cm³ in some embodiments. The porous membrane 60 having the air permeability within the range is appropriately usable for a tin film forming device. That is, the air permeability within the range allows forming a tin film at a high current efficiency. The air permeability is measured compliant with JIS L 1096-6-27-1A or ASTM-D737.

[0020] A pore percentage (porosity) of the porous membrane 60 may be 35 to 90%, or 45 to 80% in some embodiments. The pore percentage within the range allows forming the metal film at a high current efficiency. The pore percentage is a proportion of the pores contained in a unit volume. Assuming that an apparent density (bulk density) of the porous membrane 60 as ρ_1 and a true density of the porous membrane 60 (density of polymer constituting the porous membrane 60) as ρ_2 , a pore percentage p is expressed as $p = 1 - \rho_1/\rho_2$. The bulk density ρ_1 of the porous membrane 60 can be obtained from a weight and an external volume of the porous membrane 60. The true density of the porous membrane 60 can be measured by helium gas replacement method.

[0021] A tensile strength of the porous membrane 60 may be 750 to 3000 kgf/cm², or 1000 to 2400 kgf/cm² in some embodiments. The tensile strength within the range allows forming a further flat metal film. The tensile strength is measured compliant with JIS K 7127: 1999.

[0022] Tensile elongation of the porous membrane 60 may be 5 to 85% and may be 15 to 80% in some embodiments. The tensile elongation within the range allows forming a further flat metal film. The tensile elongation is measured compliant with JIS C 2151 or ASTM D882.

[0023] A thickness of the porous membrane 60 may be 5 to 175 μm and may be 12 to 150 μm in some embodiments. The thickness within the range allows forming the metal film at a high current efficiency.

[0024] As the porous membrane 60, a commercially available separator for a cell is usable. In addition to being lower in cost compared with the conventional solid electrolyte membrane having the ion-exchange functional group, the commercially available separator is expected to be further reduced in cost.

[0025] A method for manufacturing the separator usable as the porous membrane 60 mainly includes a dry method (stretch-opening method) and a wet method (phase separation method). The dry method is a method in which a film made of polymer and having a uniform composition is annealed to form a lamellar structure, then the film is uniaxially extended to cause an interface between layers in the lamellar structure to be cleaved and pores to be formed. In the porous membrane formed by the dry method, the pores linearly penetrate the porous membrane in a thickness direction of the porous membrane. Meanwhile, the wet method is a method in which a membrane formed of polymer and solvent which are microphase-separated is manufactured, and a solvent phase in this membrane is extracted and removed to cause pores to be formed. The membrane may be stretched before and/or after the extraction and removal of the solvent. In the wet method, the porous membrane having various pore structures can be manufactured by selecting a combination of the polymer and the solvent, a stretch condition, and the like. Since the pores formed by the wet method forms a three-dimensionally random and homogeneous network structure, the porous membrane obtained by the wet method has a high mechanical strength. As the porous membrane used in the film forming device according to the embodiment, the porous membrane manufactured by the wet method may be used. Since the pores in the porous membrane manufactured by the wet method form the three-dimensionally random and homogeneous network structure, the use of the porous membrane manufactured by the wet method allows suppressing a penetration and a leakage of the liquid electrolyte L containing the metal ions provided in the solution containing space 55 through the porous membrane 60.

(4) Solution Container 50

[0026] The solution container 50 usually has a hollow columnar shape having openings in its upper portion and lower portion. The porous membrane 60 is disposed so as to cover the opening in the lower portion of the solution container 50, and a lid 52 is disposed so as to cover the opening in the upper portion of the solution container 50. The anode 20

is disposed between the porous membrane 60 and the lid 52 with separated from the porous membrane 60. Thus, the solution containing space 55 is defined between the anode 20 and the porous membrane 60. The solution container 50 contains the liquid electrolyte L containing the metal ions. Although the anode 20 is in contact with the lid 52 in FIG. 1, the anode 20 and the lid 52 may be separated. In this case, the liquid electrolyte L may be also provided between the

[0027] The metal ions in the liquid electrolyte L are not specifically limited but may be ions of metal such as silver, gold, tin, and nickel. As described in examples described later, such a metal can be deposited at a high current efficiency with the film forming device 100. The metal ions may be ions of metal having a negative standard oxidation-reduction potential, that is, ions of metal less noble than hydrogen (ions of metal whose ionization tendency is higher than that of hydrogen). With the conventional solid electrolyte deposition method using the film having the ion-exchange functional group, it is especially difficult to deposit the metal having a negative standard oxidation-reduction potential at a high current efficiency. On the other hand, the film forming device 100 allows the film of the metal having the negative standard oxidation-reduction potential to be formed at a high current efficiency. Examples of the metal having the negative standard oxidation-reduction potential include tin and nickel.

[0028] When the liquid electrolyte L contains tin ions, the liquid electrolyte L contains methanesulfonic acid. For example, as the liquid electrolyte (tin solution) L containing the tin ions, a solution containing tin methanesulfonate, methanesulfonic acid, isopropyl alcohol, water, and nonionic surfactant may be used. Note that an ionic liquid may be added to the liquid electrolyte L. Examples of the ionic liquid include 1-ethyl-3-methylimidazolium bromide (EMIB), trimethyl hexyl ammonium bis (trifluoromethanesulfonyl) imide (TMHA-TFSI), 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (EMI-TFSI), TPA-TFSI, trimethylphenyl ammonium chloride (TMPAC), 1-ethyl-3-methylimidazolium chloride (EMIC), and 1-butyl pyridinium chloride (BPC). Furthermore, antioxidant and smoothing agent (for example, 2-mercaptobenzothiazole) may be added to the liquid electrolyte L. While the solid electrolyte membrane used in the conventional plating method may be dissolved in the organic solvent (such as methanesulfonic acid and isopropyl alcohol) contained in the liquid electrolyte in some cases, the porous membrane 60 used in the film forming device 100 is not dissolved in the organic solvent in the electrolyte L.

(5) Power Supply 40

[0029] The power supply 40 is electrically connected to the anode 20 and the cathode 30. The power supply 40 generates an electric potential difference between the anode 20 and the cathode 30.

<Method for Forming Metal Film>

[0030] The following describes the method for forming the metal film using the film forming device 100 (see FIG. 1). As depicted in FIG. 2, the metal film forming method includes: impregnating the porous membrane 60 with ethanol (Step S1) and applying a voltage between the anode 20 and the cathode 30 to deposit the metal on the surface of the cathode 30 (Step S2). Note that impregnating the porous membrane 60 with the ethanol (Step S1) is an optional step and is not essential. The following describes the respective steps in order.

(1) Impregnating Porous Membrane with Ethanol (S1)

[0031] The porous membrane 60 is impregnated with the ethanol to cause the ethanol to enter the pores in the porous membrane 60. This improves wettability of the porous membrane 60 by the liquid electrolyte L, which facilitates causing the liquid electrolyte L to enter the pores in the porous membrane 60 at the subsequent voltage applying step. A temperature of the ethanol during the impregnation is not specifically limited and may be in a temperature range equal to or higher than a freezing point of the ethanol and equal to or lower than 40°C.

(2) Applying Voltage (S2)

[0032] The above-described solution containing space 55 in the film forming device 100 is filled with the liquid electrolyte L containing the metal ions. Additionally, the porous membrane 60 is brought into contact with the cathode 30. In this state, a voltage is applied between the anode 20 and the cathode 30 by the power supply 40. The metal ions in the liquid electrolyte L move in a direction from the anode 20 to the cathode 30 through the porous membrane 60. The metal ions reach an interface (surface) 30a between the porous membrane 60 and the cathode 30 and are reduced to turn into metal deposit. Thus, the metal film is formed on the cathode 30.

[0033] When the voltage is applied, the porous membrane 60 may be heated. For example, heating of the cathode 30 allows indirect heating of the porous membrane 60, but the method for heating the porous membrane 60 is not limited to this. Heating the porous membrane 60 reduces viscosity of the ethanol in the pores in the porous membrane 60, and

the liquid electrolyte L is likely to enter the pores in the porous membrane 60. The heating temperature is not specifically limited provided that the heating temperature is equal to or lower than the boiling point of the ethanol and equal to or lower than the melting point of the porous membrane 60. The heating temperature may be, for example, 35 to 65°C.

[0034] When the voltage is applied, a pressure in the solution containing space 55 may be increased, which facilitates causing the liquid electrolyte L in the solution containing space 55 to enter the pores in the porous membrane 60. The pressure in the solution containing space 55 may be, for example, 0.5 to 3 MPa.

[0035] The voltage may be applied with the porous membrane 60 being pressed against the cathode 30 at a predetermined pressure. This can improve the flatness of the formed metal film. For example, a pressure of 0.5 to 3 MPa may be applied.

[0036] Besides, various film forming conditions such as the applied voltage may be appropriately set depending on a formed film area, a targeted film thickness, and the like.

[0037] When the metal ions are hydrated, the porous membrane 60 composed of a hydrophobic polyolefin chain is less wettable by the electrolyte L containing the metal ions.

[0038] The pores in the porous membrane 60 need not be uniform in diameter, but may vary in diameter. In the film formation using the film forming device 100, the pores in the porous membrane 60 are filled with the ethanol before the film formation. Increasing the pressure in the solution containing space 55 at the film formation causes the ethanol in the pores having the larger pore diameters to be pushed out and substituted with the liquid electrolyte L, which allows the liquid electrolyte L to move from the solution containing space 55 to the cathode 30 through the porous membrane 60.

[0039] While the embodiments of the present disclosure have been described in detail above, the present disclosure is not limited thereto, and can be subjected to various kinds of changes in design without departing from the spirit of the present disclosure described in the claims.

EXAMPLES

[0040] While the following further specifically describes the present disclosure through examples and comparative examples, the present disclosure is not limited to these examples.

Examples 1 to 5

(1) Manufacturing Nickel SED Substrate

[0041] A copper-sputtered substrate where a copper-sputtered film was formed on an AlSi substrate was prepared. A nickel film was formed on this copper-sputtered substrate by solid electrolyte deposition method. Conditions for the solid electrolyte deposition were as follows. A nickel film forming area was defined by disposing a polyimide tape (Kapton adhesive tape: 650R#25 manufactured by Teraoka Seisakusho co., Ltd.) having an opening of 10 × 10 mm on the copper-sputtered substrate. The nickel film formed on the copper-sputtered substrate by the solid electrolyte deposition method had a thickness of 4 μm. The nickel solid electrolyte deposition (SED) substrate was thus obtained, and used as a substrate for forming a tin film thereon.

[0042] Anode: nickel porous body

Cathode: copper-sputtered substrate

Solid electrolyte membrane: Nafion 117 (manufactured by DuPont)

Liquid electrolyte: nickel solution obtained by mixing nickel chloride aqueous solution and acetic acid (pH 4.0)

Temperature of copper-sputtered substrate: 60°C

Pressure of pressing the solid electrolyte membrane against the copper-sputtered substrate: 1 MPa

Current density: 100 mA/cm²

Nickel film forming area: 10 mm × 10 mm

(2) Preparing Liquid Electrolyte Containing Tin Ions (Tin Solution)

[0043] 150 g of nonionic surfactant (manufactured by Merck KGaA, copolymer of propylene oxide/ethylene oxide) was mixed with 200 g of isopropyl alcohol to obtain a mixed solution. Tin methanesulfonate was added to the mixed solution such that the mixed solution had a divalent tin ion concentration of 60 g/L, and the mixed solution was stirred. Furthermore, methanesulfonic acid was added such that the mixed solution had a free acid concentration (methanesulfonic acid concentration) of 1.0 M, and the mixed solution was stirred. Afterwards, 500 g of water was added to obtain 1000 g of tin solution.

(3) Preparing Porous Membrane

[0044] In each example, a commercially available separator for lithium-ion battery (manufactured by Toray Industries, Inc., product name: SETELA) was prepared as the porous membrane. Each of these porous membranes was composed of polyolefin chains. A pore diameter, air permeability, a tensile strength, a tensile elongation, a pore percentage, and a thickness of each porous membrane were as described in Table 1. A ratio of the number of oxygen atoms to that of carbon atoms in each porous membrane measured by X-ray photoelectron spectroscopic measurement device (PHI-5800 manufactured by ULVAC-PHI, Inc.) was 0.01 to 0.02. By immersing these porous membranes into ethanol, the porous membrane was impregnated with the ethanol.

(4) Forming Tin Film

[0045] Using a nickel SED substrate as a cathode (substrate) and a tin foil (SN-443261, manufactured by Nilaco Corporation) as an anode, the substrate and the tin foil were oppositely disposed. The porous membrane was disposed between the substrate and the tin foil so as to be in contact with the substrate. A space between the porous membrane and the tin foil was filled with the tin solution. Thus, the film forming device as illustrated in FIG. 1 was constituted.

[0046] The porous membrane was heated through heating the substrate to 40°C, and a voltage was applied between the cathode and the anode to cause a current to flow with a current density of 20 mA/cm² while the porous membrane pressed against the substrate at 0.50 MPa. As a result, the tin was deposited on the substrate to form a tin film. The tin film forming area had a size of 10 × 10 mm. The tin film forming area was defined using the polyimide tape similarly to the nickel film formation.

[0047] In each example, a weight of the tin deposited on the substrate was measured. By obtaining a ratio of the measured value to a theoretical deposition amount calculated from the Faraday's law, a current efficiency of the tin film formation was calculated. Table 1 depicts the obtained values of the current efficiencies. A thickness of the tin film obtained from the theoretical deposition amount was 4 μm.

Comparative Examples 1 to 5

[0048] Nafion solution (manufactured by DuPont) was casted and spread on a flat plate to form an ion-exchange membrane by casting method. Using this ion-exchange membrane instead of the porous membrane, a tin film was formed similarly to Examples 1 to 5. Table 1 depicts pore diameters, air permeabilities and equivalent weights (weights of dried resin films corresponding to one equivalent of ion-exchange functional group) of the ion-exchange membranes used in Comparative Examples 1 to 5. Similarly to Examples 1 to 5, the current efficiency in each Comparative Example was obtained. Table 1 depicts the obtained values of the current efficiencies.

[0049] Compared with Comparative Examples 1 to 5, Examples 1 to 5 where the pore diameters were within the range of 27 to 1000 nm and the air permeabilities were within the range of 10 to 260 s/100 cm³ all exhibited the high current efficiencies.

(Table 1)

	Pore Diameter [nm]	Air Permeability [s/100 cm ³]	Tensile Strength [kgf/cm ²]	Tensile Elongation [%]	Pore Percentage [%]	Thickness [μ m]	Equivalent Weight [g/eq]	Current Efficiency [%]
Example 1	27	260	1500	40	47	25	-	100
Example 2	31	170	1300	80	45	100	-	95
Example 3	50	60	2303	60	55	150	-	100
Example 4	200	40	1422	15	70	12	-	100
Example 5	1000	10	1030	30	80	30	-	100
Comparative Example 1	4	1000	500	50	37	50	874	60
Comparative Example 2	4	993	385	13	39	24	812	65
Comparative Example 3	4	993	485	6	37	25	879	65
Comparative Example 4	4	1001	380	20	39	58	946	65
Comparative Example 5	4	997	330	25	40	50	735	62

Examples 6 to 10

(1) Preparing Liquid Electrolyte (Nickel Solution) Containing Nickel Ions

[0050] 222 g of nickel chloride hexahydrate and 124 g of nickel acetate tetrahydrate were dissolved in ion-exchange water to a total amount of 950 mL. While pH of this solution was measured, acetic acid was added dropwise such that the pH fell within the range of 3.85 to 3.95. Further, the solution was diluted with ion-exchange water to a total amount of 1000 mL. The obtained solution was used as a nickel solution.

(2) Preparing Porous Membrane

[0051] A porous membrane (manufactured by Toray Industries, Inc.) composed of the polyolefin chain and having the pore diameter described in Table 2 was prepared for each example. A ratio of the number of oxygen atoms to that of carbon atoms in each porous membrane measured by X-ray photoelectron spectroscopic measurement device (PHI-5800 manufactured by ULVAC-PHI, Inc) was 0.01 to 0.02. By immersing the porous membrane with ethanol, the ethanol was caused to enter the pores in the porous membrane.

(3) Forming Nickel Film

[0052] A copper plate was subjected to an activation treatment by a dip into a 10% aqueous solution of sulfuric acid at room temperature for 10 minutes. Using the copper plate as a cathode (substrate) and using a nickel porous body as an anode, the copper plate and the nickel porous body were oppositely disposed. The porous membrane was disposed between the copper plate and the nickel porous body so as to be in contact with the copper plate. A space between the porous membrane and the nickel porous body was filled with the nickel solution. Thus, the film forming device as illustrated in FIG. 1 was constituted.

[0053] Next, the porous membrane was heated through heating the copper plate to 60°C, and a voltage was applied between the cathode and the anode to cause a current to flow with a current density of 75 mA/cm² while the porous membrane pressed against the copper plate at 1.0 MPa. As a result, the nickel was deposited on the copper plate to form a nickel film. The nickel film forming area had a size of 10 × 20 mm. The nickel film forming area was defined using the polyimide tape similarly to Examples 1 to 5.

[0054] In each example, a weight of the nickel deposited on the copper plate was measured. By obtaining a ratio of the measured value to a theoretical deposition amount calculated from the Faraday's law, a current efficiency of the nickel film formation was calculated. Table 2 depicts the obtained values of the current efficiencies. FIG. 3 illustrates a relationship between the pore diameter and the current efficiency in the nickel film formation. A thickness of the nickel film obtained from the theoretical deposition amount was 5 μm.

Comparative Example 6

[0055] Using an ion-exchange membrane (product name: Nafion) manufactured by DuPont instead of the porous membrane, a nickel film was formed similarly to Examples 6 to 10. The ion-exchange membrane had a pore diameter of 1 nm. Similarly to Examples 6 to 10, a current efficiency of the nickel film formation in Comparative Example 6 was obtained. Table 2 depicts the results. FIG. 3 indicates the current efficiency of Comparative Example 6 by the dashed line.

[0056] The current efficiencies of Examples 6 to 10 were higher than that of Comparative Example 6. Additionally, as illustrated in FIG. 3, the pore diameter and the current efficiency exhibited a positive correlation when the pore diameter was 50 nm or less. Meanwhile, the pore diameter and the current efficiency did not exhibit the positive correlation when the pore diameter was 50 nm or more. These results were seemingly due to an influence of capillarity being small when the pore diameter was 50 nm or more.

(Table 2)

	Pore Diameter [nm]	Current Efficiency [%]
Example 6	30	52.7
Example 7	31	52.7
Example 8	48	90
Example 9	50	98.9
Example 10	100	52.7

(continued)

	Pore Diameter [nm]	Current Efficiency [%]
Comparative Example 6	1	45

DESCRIPTION OF SYMBOLS

[0057]

- 20 Anode
- 30 Cathode
- 40 Power supply
- 50 Solution container
- 55 Solution containing space
- 60 Porous membrane
- 100 Film forming device
- L Liquid electrolyte

Claims

1. A film forming device (100) for forming a metal film comprising:

an anode (20);
a cathode (30);
a porous membrane (60) disposed between the anode (20) and the cathode (30) to be capable of contacting the cathode (30);
a solution container (50) defining a solution containing space between the anode (20) and the porous membrane (60); and
a power supply (40) applying a voltage between the anode (20) and the cathode (30),
wherein the porous membrane (60) is composed of a polyolefin chain without an ion-exchange functional group.

2. The film forming device (100) according to claim 1,
wherein the porous membrane (60) has a pore diameter within a range of 20 to 2000 nm.

3. The film forming device (100) according to claim 1 or 2,
wherein the porous membrane (60) has air permeability within a range of 5 to 500 s/100 cm³.

4. A method for forming a film of metal comprising
applying a voltage between the anode (20) and the cathode (30) in the film forming device (100) according to any one of claims 1 to 3 in a state where the solution containing space is filled with a liquid electrolyte (L) containing ions of the metal and the porous membrane (60) is in contact with the cathode (30).

5. The method according to claim 4,
wherein the metal has a negative standard oxidation-reduction potential.

6. The method according to claim 4 or 5, further comprising

impregnating the porous membrane (60) with ethanol,
wherein the voltage is applied between the anode (20) and the cathode (30) while the porous membrane (60) is heated.

7. The method according to any one of claims 4 to 6,
wherein the metal is tin or nickel.

8. The method according to claim 7,
wherein the metal is the tin, and the liquid electrolyte (L) contains methanesulfonic acid.

Fig. 1

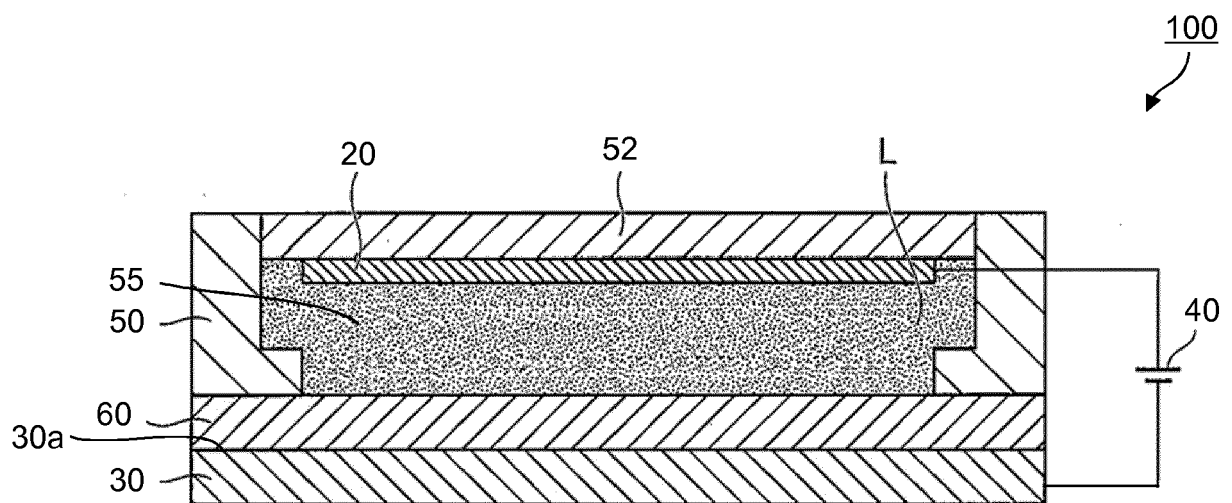


Fig. 2

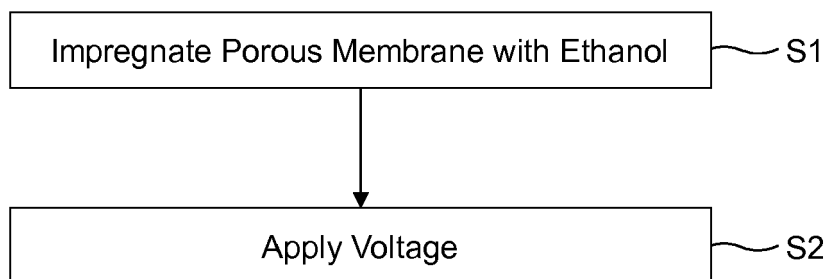
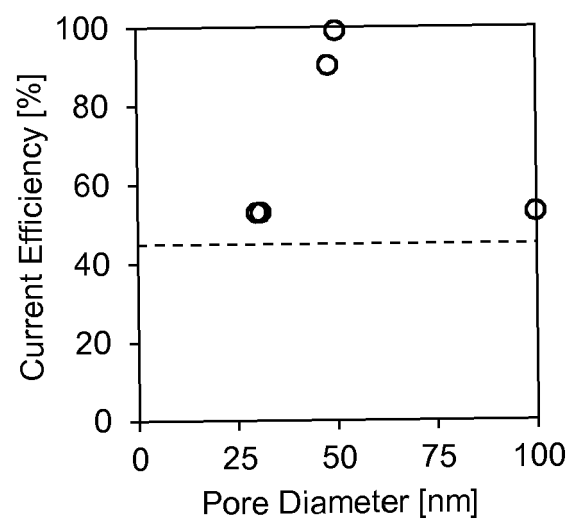


Fig. 3



REFERENCES CITED IN THE DESCRIPTION

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