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**Nakano**

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(54) **REFERENCE ELECTRODE**

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(52) **U.S. Cl.**

CPC ..... **G01N 27/414** (2013.01); **G01N 27/301** (2013.01)

(58) **Field of Classification Search**

None  
See application file for complete search history.

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(57) **ABSTRACT**

A reference electrode including a casing through which one face at one side of a liquid junction that leaches an internal liquid is exposed, the casing being provided with an overhang portion that hangs out on the one face side of the liquid junction and prevents separation of the liquid junction from the casing; and an open portion that leaves a space on the one side of the liquid junction open toward a lateral direction along the one face.

**3 Claims, 9 Drawing Sheets**

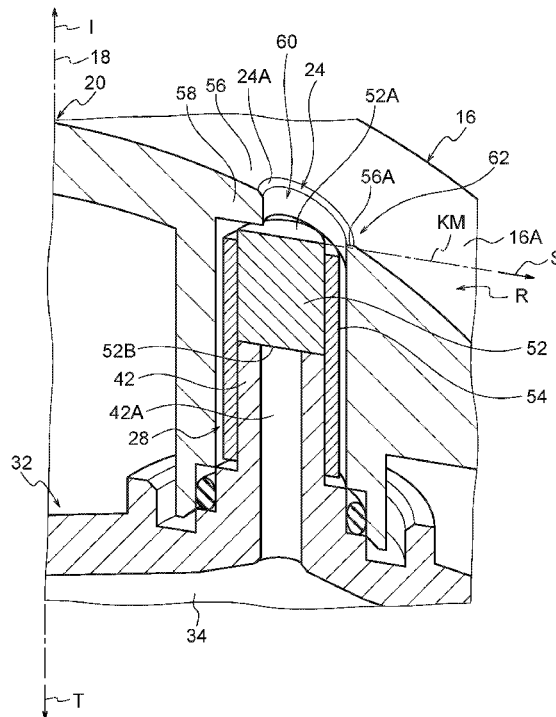


FIG. 1

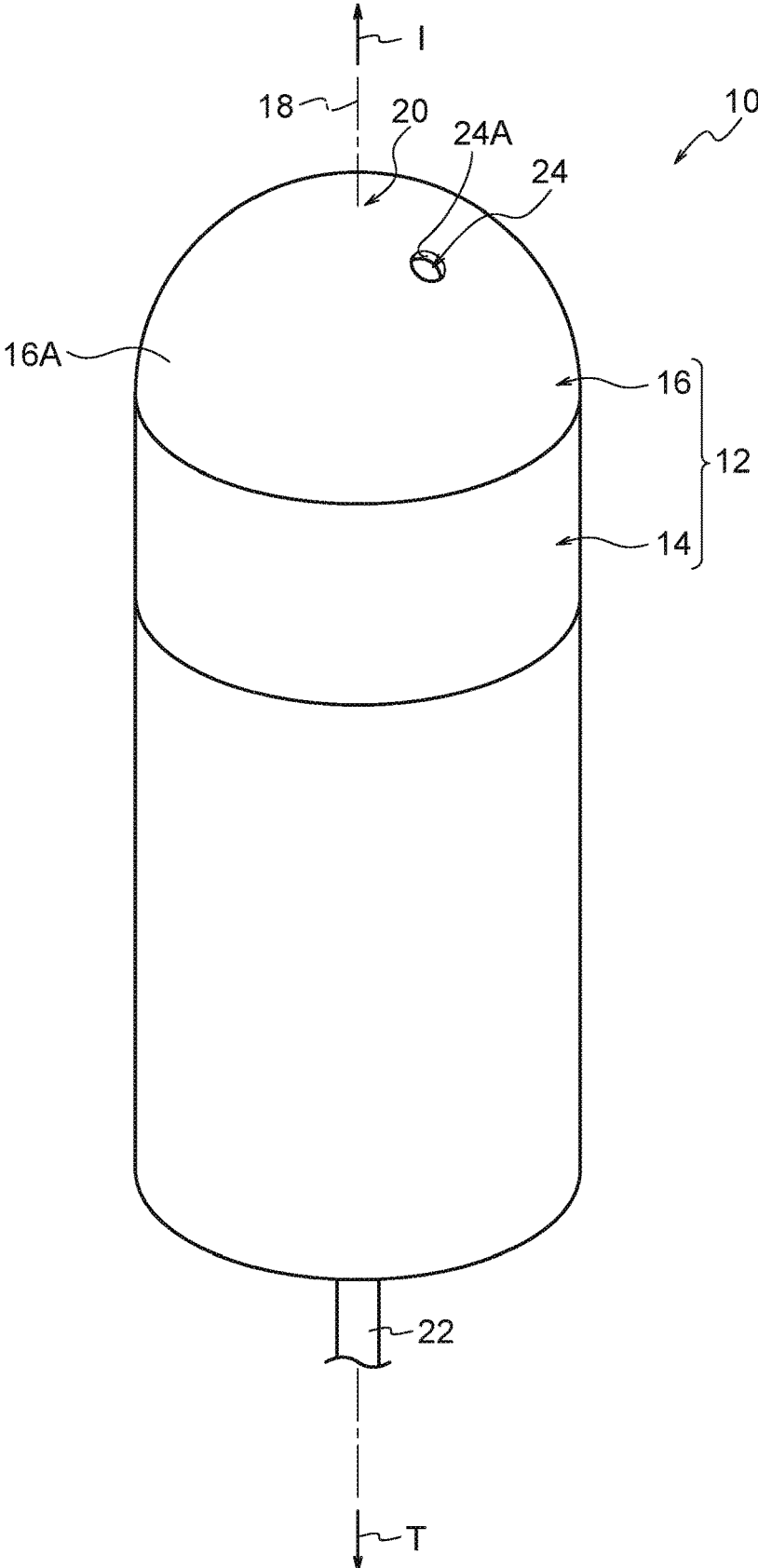




FIG.3

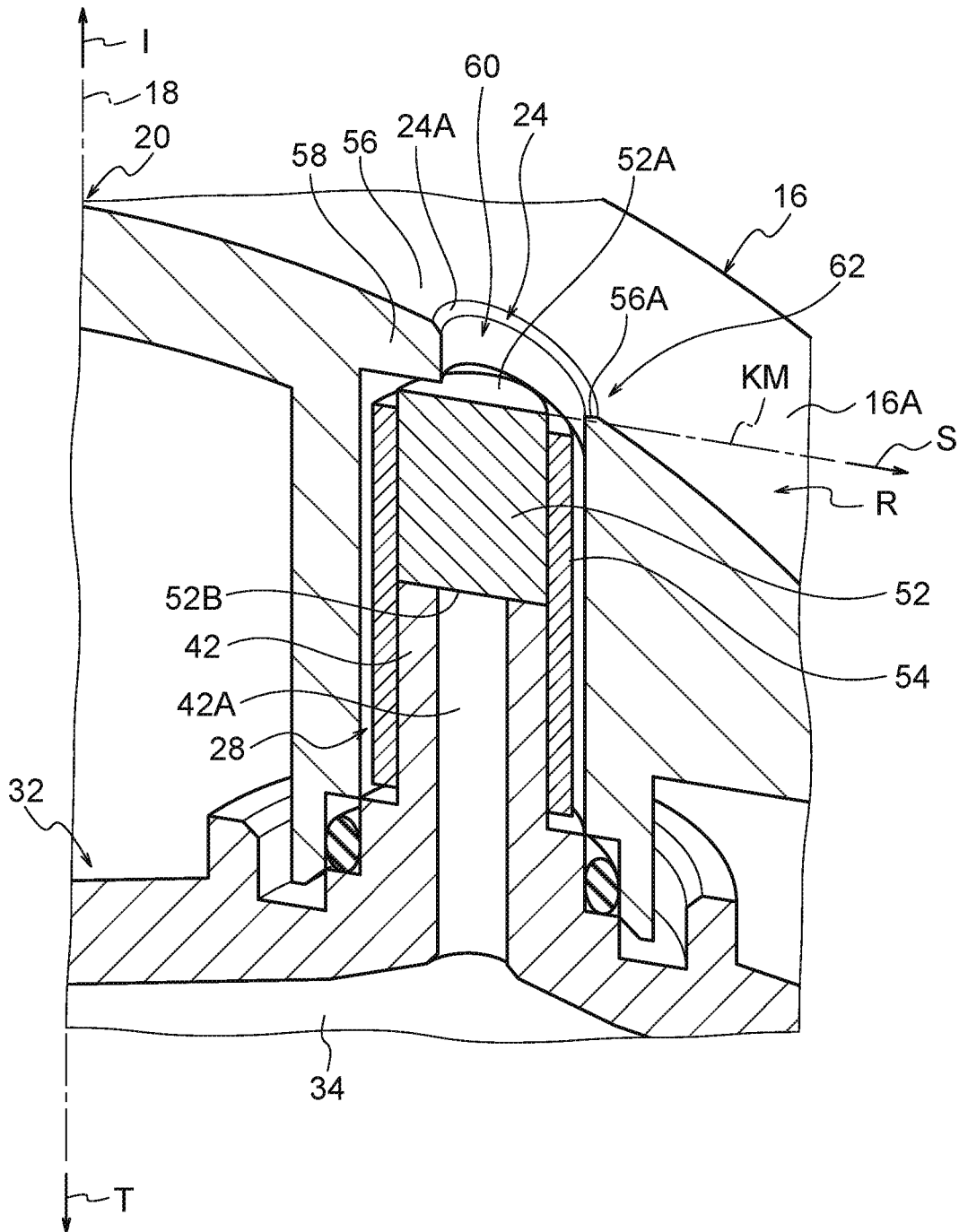


FIG. 4

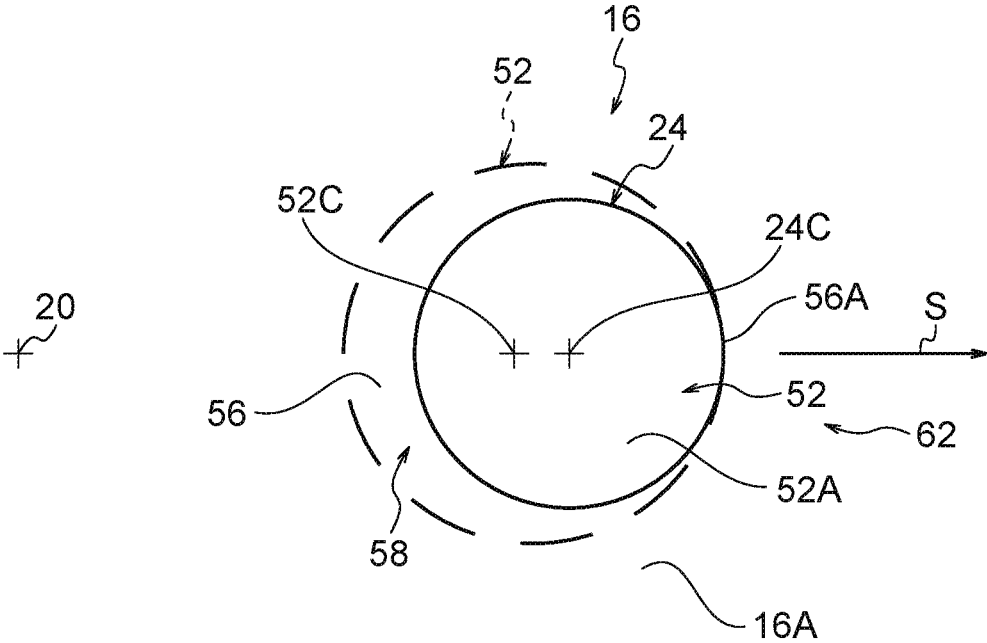
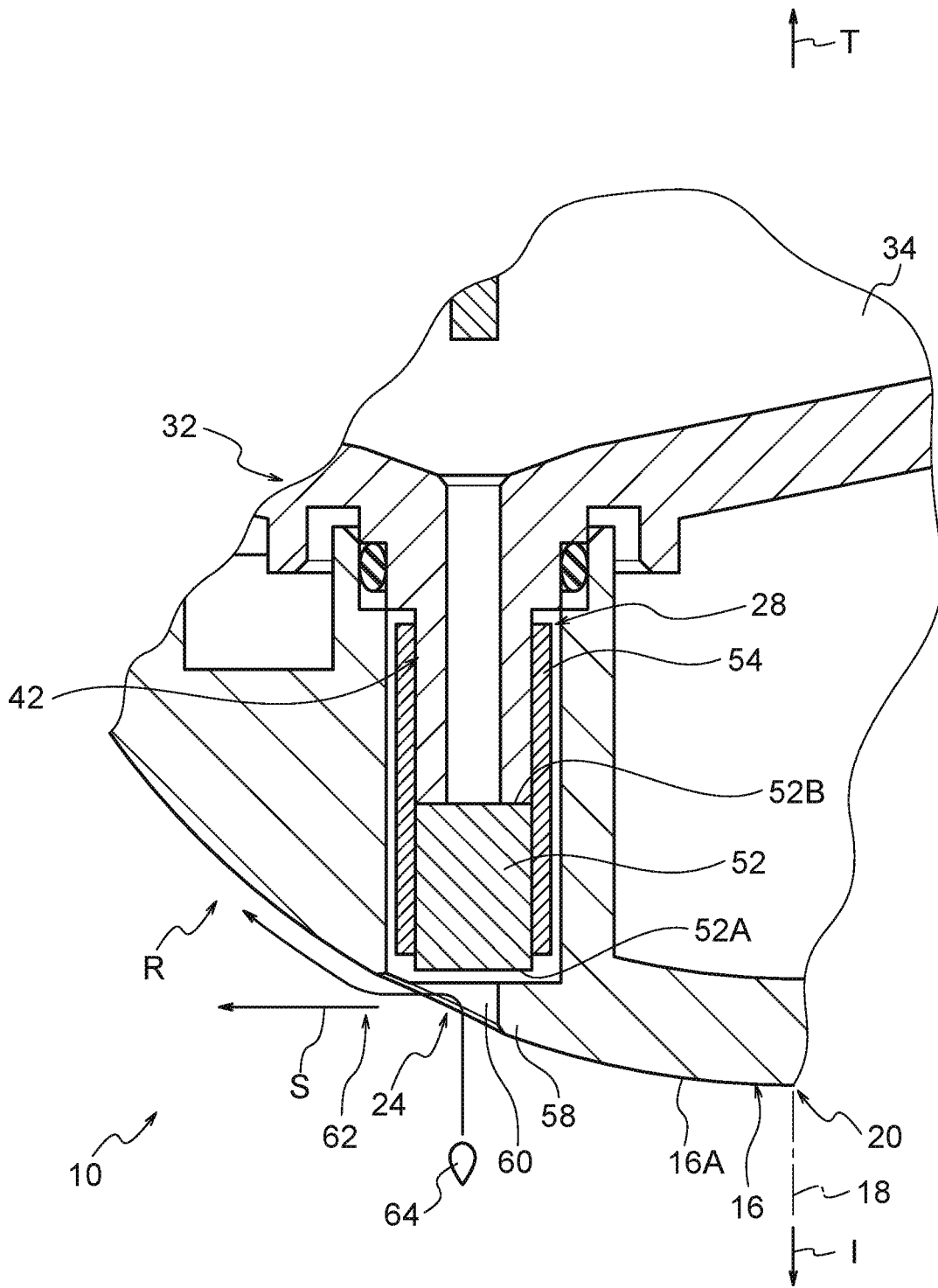


FIG. 5



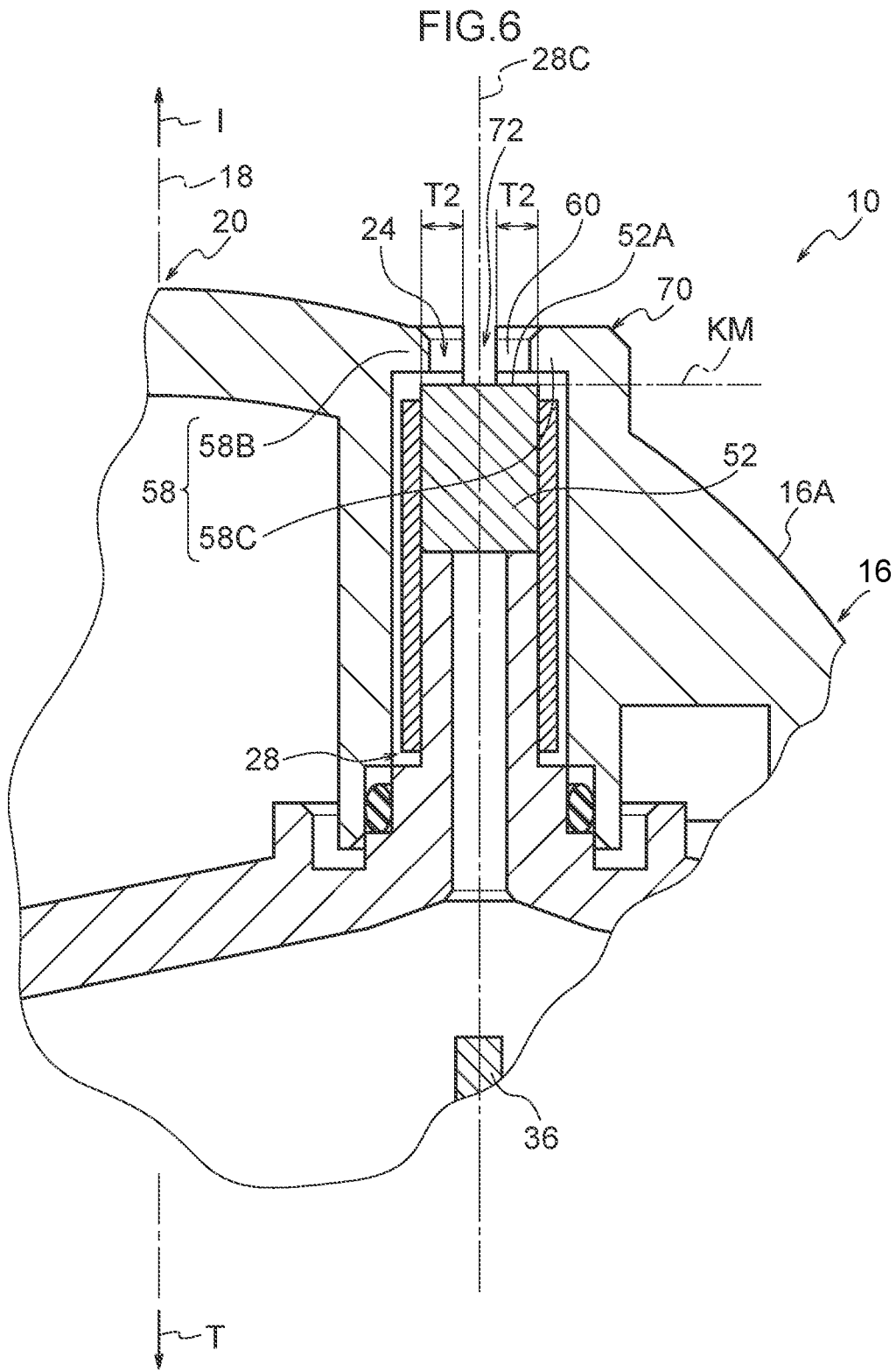






FIG. 8

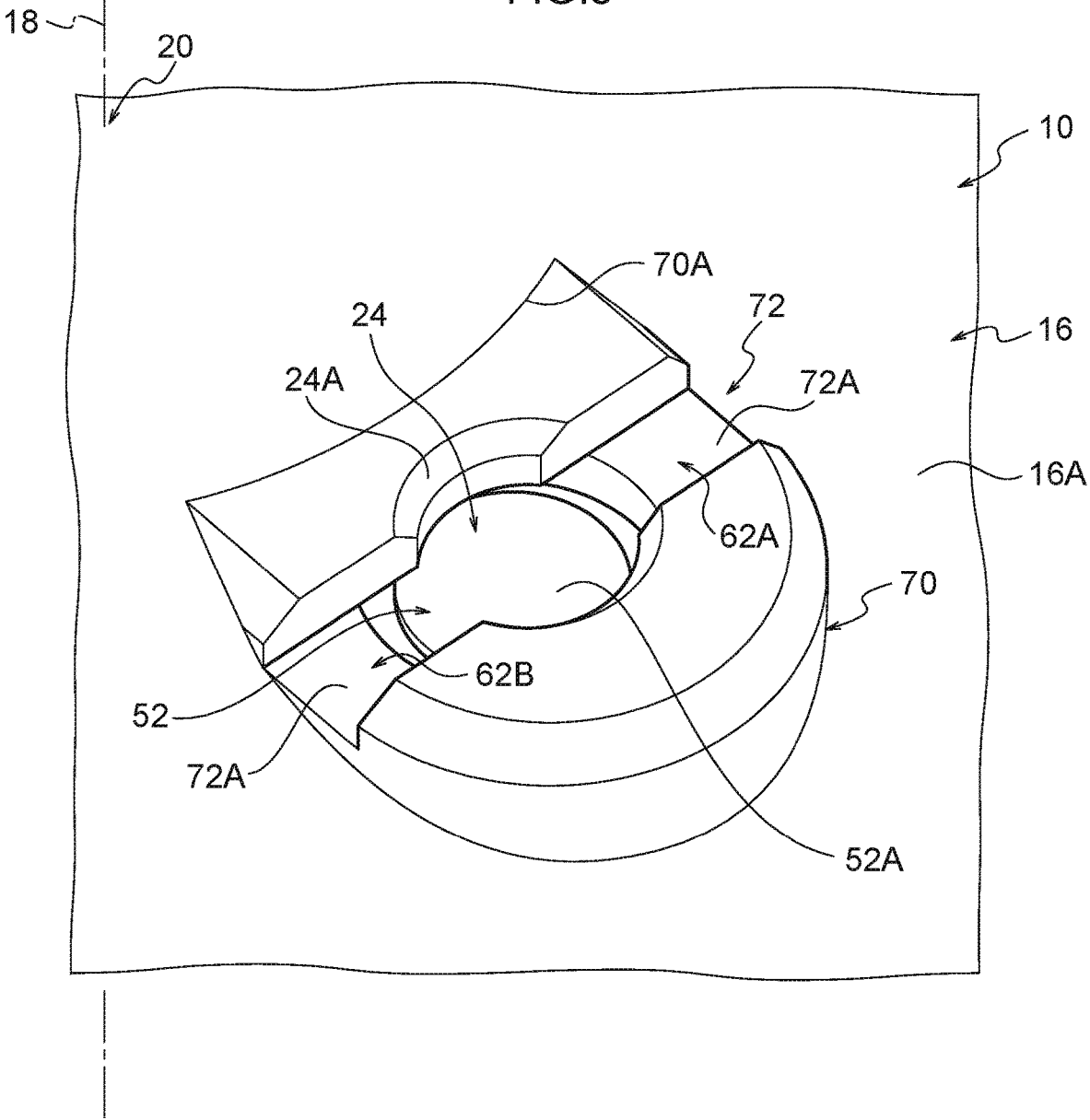
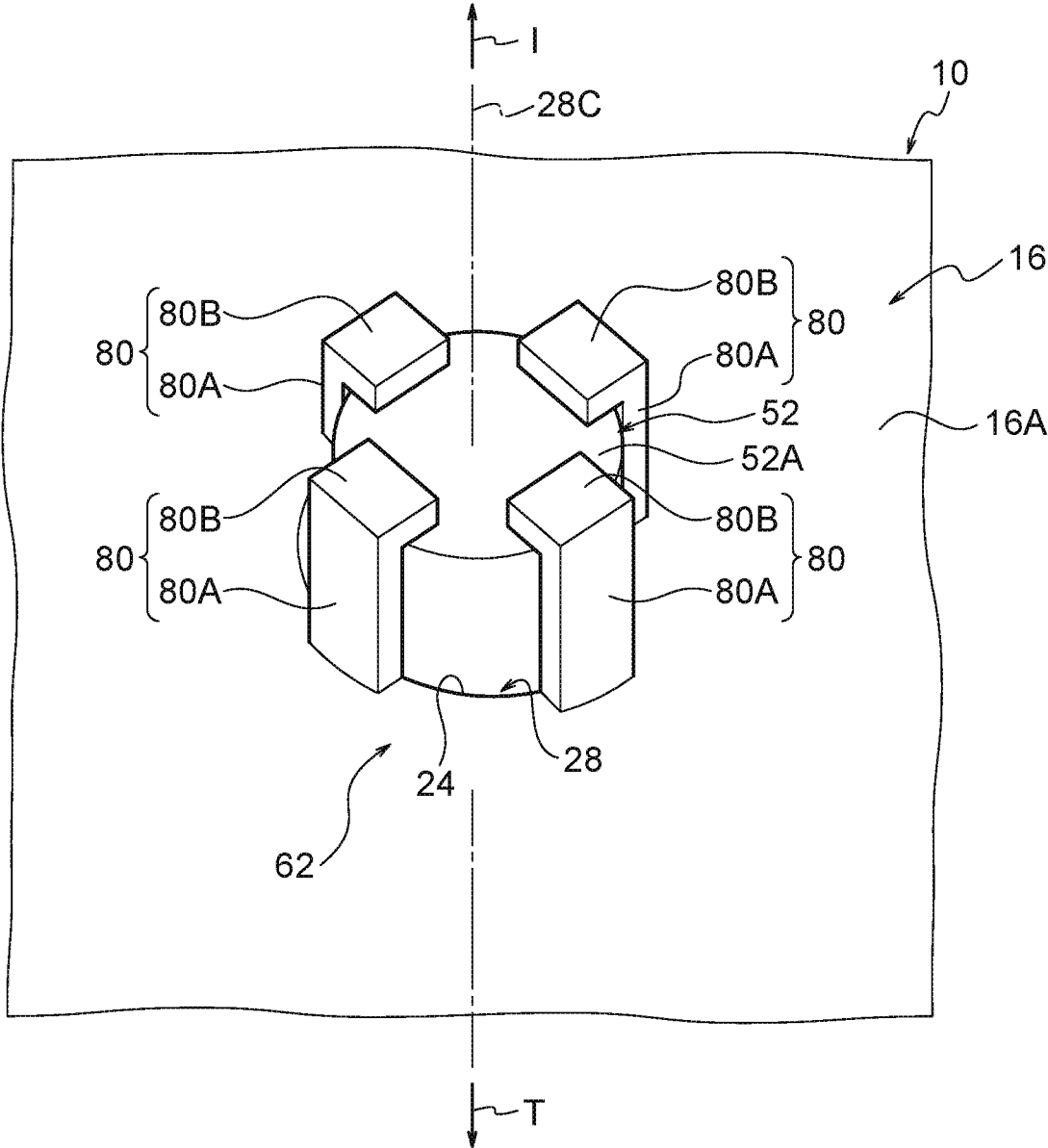


FIG. 9



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## REFERENCE ELECTRODE

## CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation application of application Ser. No. 16/171,631 filed on Oct. 26, 2018, now U.S. Pat. No. 11,073,496 issued on Jul. 27, 2021, which application claims priority under 35 USC 119 from Japanese Patent Application No. 2017-208552 filed on Oct. 27, 2017, the disclosure of which is incorporated by reference herein.

## BACKGROUND

## Technical Field

The present disclosure relates to a reference electrode employed to inspect a given place.

## Related Art

Known methods of measuring, for example, the pH at a given place include methods which employ an ISFET. This ISFET measures pH based on the electric potential of a reference electrode.

Such reference electrodes are configured with an internal electrode including silver/silver chloride or the like that is immersed in a potassium chloride solution, with the potassium chloride solution being in contact with a substance to be measured via a liquid junction including a porous material.

Japanese Patent Application Laid-Open (JP-A) No. 2012-47647 illustrates one known reference electrode. A liquid junction is provided at a leading end portion of a support tube of this reference electrode. A cylindrical membrane-fixing member is screwed onto the leading end portion of the support tube, and the liquid junction is fixed in place in a state in which a circumferential edge portion of the liquid junction is held between the support tube and a flange portion provided at an end portion of the membrane-fixing member.

In such a reference electrode, a space at the surface of the liquid junction is surrounded by the flange portion. Accordingly, when the leading end portion of the reference electrode is, for example, inserted into a nutrient liquid and pH is measured, bubbles accumulate in the space surrounded by the flange portion.

In such cases, the liquid junction may not be able to make contact with the nutrient liquid, and measurement results may become unstable.

## SUMMARY

In view of the above circumstances, the disclosure provides a reference electrode capable of stabilizing measurement results.

A reference electrode according to the disclosure includes a casing through which one face at one side of a liquid junction that leaches an internal liquid is exposed. The casing is provided with an overhang portion and an open portion. The overhang portion hangs out on the one face side of the liquid junction and prevents separation of the liquid junction from the casing. The open portion leaves a space on the one side of the liquid junction open in a lateral direction along the one face.

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The disclosure enables measurement results to be stabilized compared with cases in which a surface of a liquid junction is surrounded by a flange.

## BRIEF DESCRIPTION OF THE DRAWINGS

Exemplary embodiments of the present disclosure will be described in detail based on the following figures, wherein:

FIG. 1 is a perspective view illustrating a reference electrode according to a first embodiment;

FIG. 2 is a cross-sectional view illustrating relevant parts of FIG. 1;

FIG. 3 is a perspective cross-sectional view corresponding to FIG. 2;

FIG. 4 is a plan view illustrating an opening according to a first embodiment;

FIG. 5 is an explanatory diagram illustrating an effect according to the first embodiment;

FIG. 6 is a cross-sectional view illustrating relevant parts, corresponding to that in FIG. 2, of a reference electrode according to a second embodiment;

FIG. 7 is a perspective cross-sectional view corresponding to FIG. 5;

FIG. 8 is a perspective view illustrating relevant parts of a reference electrode according to the second embodiment; and

FIG. 9 is a perspective view illustrating relevant parts of a reference electrode according to a third embodiment.

## DETAILED DESCRIPTION

## First Embodiment

Explanation follows regarding a first embodiment, with reference to the drawings. FIG. 1 is a diagram illustrating a reference electrode 10 according to a first embodiment. The reference electrode 10 is, for example, when measuring the pH of soil or a hydroponic nutrient liquid for raising crops.

The reference electrode 10 is employed in combination with an ion-sensitive field-effect transistor (ISFET), this being a measurement sensor. The ISFET measures pH based on the electric potential of the reference electrode 10. The ISFET may be provided at any place in a casing 12 of the reference electrode 10.

Soil or nutrient liquid pH values are managed on the basis of these measurement values to create an environment suited to crop growth.

The casing 12 of the reference electrode 10 is provided with a bottomed, cylindrical body 14 and a hemispherical head 16. The head 16 is provided at one side I of the body 14, and closes off an opening in a leading end of the body 14. An apex 20 of the head 16 of the casing 12 is defined at a location positioned on a center line 18 of the casing 12 where the head 16 projects furthest toward the one side I. A head surface 16A curves toward another side T, this being on the body 14 side of the head 16, on progression from the apex 20 toward an outer circumferential portion. A cable 22 for communication extends out from a base end of the body 14 of the casing 12, this being a bottom portion of the body 14.

In use, the reference electrode 10 is buried in soil or inserted into a nutrient liquid with the head 16 pointed downward. An opening 24 is formed at a location on the head 16 offset toward an outer circumferential side from the apex 20. An edge of the opening 24 is beveled to form a beveled portion 24A.

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As illustrated in FIG. 2, a projection 26 that projects toward the inside of the casing 12 is formed to the backside of the head 16 where the opening 24 is provided. A circular seating hole 28 is formed in the projection 26. In FIG. 2, the one side I of the seating hole 28, indicating an upper side, is in communication with the outside via the opening 24. Also in FIG. 2, the another side T of the seating hole 28, indicating a lower side, is open. A mounting hole 30 is formed in an end face of the projection 26 so as to surround the seating hole 28.

A container-shaped tank 32 is provided inside the casing 12 of the reference electrode 10. The inside of the tank 32 is filled with an internal liquid 34. An internal electrode 36 is disposed in the internal liquid 34. The internal electrode 36 is connected to a non-illustrated controller. Examples of the internal liquid 34 include a potassium chloride (KCl) solution, and examples of the material of the internal electrode 36 include silver/silver chloride (Ag/AgCl).

A ring portion 40 that projects in a ring shape is formed to an upper face 38 of the tank 32. A cylindrical tube portion 42 extends out toward the one side I from a central portion of the ring portion 40. A communication hole 42A inside the tube portion 42 is in communication with the inside of the tank 32. The communication hole 42A is configured such that the internal liquid 34 inside the tank 32 is able to be supplied from a leading end of the tube portion 42.

An inner face 38A of the upper face 38 of the tank 32 is inclined toward the one side I, this being the leading end side of the tube portion 42, on progression from the outer circumferential portion to the communication hole 42A. The communication hole 42A is disposed along an extension line 44 from the internal electrode 36, and the liquid junction 52 is also disposed along the extension line 44. Thus, when the reference electrode 10 is used with the head 16 pointed downward, configuration is such that the internal liquid 34 collects in the communication hole 42A, and configuration is such that the internal electrode 36 touches the internal liquid 34 that has collected in the communication hole 42A even in a state in which the internal liquid 34 has been reduced.

A thick portion 46 that is thicker than the tube portion 42 is formed to a base end portion of the tube portion 42 on the tank 32 side of the tube portion 42. A large-diameter portion 48 that has a larger diameter than the thick portion 46 is formed on the base end side of the thick portion 46. A step 48A is thus formed between the large-diameter portion 48 and the thick portion 46, restricting the amount of intrusion of an O-ring 50 that is fitted to the outside of the thick portion 46.

The liquid junction 52 is configured from a porous material having a circular column shape, and is provided at the leading end of the tube portion 42. The outer diameter of the liquid junction 52 has substantially the same dimensions as the outer diameter of the tube portion 42, and is set from 1 mm to 5 mm. The tube portion 42 and the liquid junction 52 are surrounded by heat-shrink tubing 54. The tubing 54 shrinks when heat is applied thereto, whereby the tube portion 42 and the liquid junction 52 are fixed together by the tubing 54 without employing an adhesive agent.

In this fixed state, one face 52A on the one side I of the liquid junction 52 is exposed, and another face 52B on the another side T of the liquid junction 52 abuts an end face of the tube portion 42 of the tank 32. Configuration is thus such that internal liquid 34 from the tube portion 42 of the tank 32 is able to be supplied to the liquid junction 52 from the another face 52B and leached from the one face 52A.

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The tube portion 42 to which the liquid junction 52 is attached is inserted into the seating hole 28 from the inside of the head 16, and the liquid junction 52 is seated in the seating hole 28. In this state, the thick portion 46 provided to the base end portion of the tube portion 42 is inserted into the mounting hole 30 provided in the projection 26 of the head 16, and the O-ring 50 fitted to the outside of the thick portion 46 is placed in close contact with an outer circumferential face of the thick portion 46 and an inner circumferential face of the mounting hole 30, thus ensuring liquid-tightness.

The one face 52A of the liquid junction 52 is disposed in close proximity to the opening 24 provided in the head 16. As also illustrated in FIG. 3, the one face 52A on the one side I of the liquid junction 52 that leaches the internal liquid 34 is exposed to the head 16 configuring the casing 12. Configuration is thus such that the internal liquid 34 is able to be leached into soil or a nutrient liquid, these being substances being measured, via the liquid junction 52.

As illustrated in FIG. 4, the one face 52A of the liquid junction 52 formed in a circular column shape is circular, and the opening 24 that exposes the one face 52A is also circular. A center 52C of the circularly formed one face 52A and a center 24C of the circularly formed opening 24 are disposed at positions offset from one another. The opening 24 is eccentrically disposed with respect to the one face 52A, in a direction toward the outer circumferential side and away from the apex 20 of the casing 12.

As illustrated in FIGS. 2 to 4, part of an opening edge 56 of the opening 24 hangs out over the liquid junction 52 and covers the one face 52A of the liquid junction 52. Thus, an overhang portion 58 that hangs out across the one face 52A of the liquid junction 52 and prevents separation of the liquid junction 52 from the seating hole 28 is formed by the opening edge 56 of the opening 24.

As illustrated in FIGS. 2 and 3, the opening 24 is established in the spherically formed head surface 16A. On the opening edge 56 of the opening 24, locations toward the outer circumferential side away from the apex portion 20 are positioned on the another side T of locations on the apex portion 20 side of the opening 24.

Thus, when an imaginary plane KM is envisaged making surface contact with the one face 52A of the liquid junction 52, a rounded surface region R that does not project to the one side I of the imaginary plane KM is formed at the outer circumferential side of an outermost location 56A on the opening edge 56 furthest away from the apex 20. Due to this rounded surface region R, an open portion 62 that leaves a space 60 on the one side I of the liquid junction 52 open in a lateral direction S along the one face 52A is formed in the head surface 16A. Note that in the present embodiment, configuration is such that the outermost location 56A on the opening edge 56 is positioned on the imaginary plane KM.

As illustrated in FIG. 2, the outermost location 56A is positioned on the another side T of an inner face 58A on the liquid junction 52 side of the overhang portion 58, and the inner face 58A of the overhang portion 58 is positioned on the one side I of the imaginary plane KM. Thus, even in cases in which the amount that the liquid junction 52 is inserted into the seating hole 28 fluctuates due to mold tolerance or the like, configuration is such that the outermost location 56A is able to maintain a state positioned on the another side T of the one face 52A of the liquid junction 52.

Note that in a state in which the liquid junction 52 has been inserted to the bottom of the seating hole 28 and the one face 52A abuts the inner face 58A of the overhang portion

**58**, the one face **52A** of the liquid junction **52** is positioned on the one side I of the outermost location **56A**.

#### Operation and Effects

Explanation follows regarding the operation of the present embodiment.

As illustrated in FIG. 5, when measuring the pH of a hydroponic nutrient liquid, the head **16** of the reference electrode **10** is inserted into the nutrient liquid pointed downward. The liquid junction **52** provided to the head **16** is provided at a position set back from the head surface **16A**, and the recessed space **60** is formed on the one side I of the liquid junction **52**. As a result, when the space **60** is surrounded by a flange, bubbles **64**, which have been accumulated in the space, can not escape.

However, in the present embodiment, the head **16** configuring the casing **12** is formed with the open portion **62** that leaves the space **60** on the one side I of the liquid junction **52** open in the lateral direction S along the one face **52A**. Accordingly, even if bubbles **64** have entered into the space **60**, the bubbles **64** are able to be released from the open portion **62** along the lateral direction S.

Thus, since the internal liquid **34** is able to be leached into the nutrient liquid from the liquid junction **52**, measurement results employing the reference electrode **10** are able to be stabilized compared with cases in which the bubbles **64** impede leaching of the internal liquid **34** into the nutrient liquid.

It is thought that if the diameter of the liquid junction **52** is increased such that the surface area of the one face **52A** is made sufficiently large, it would be possible to reduce the effect of bubbles **64** on measurement results even if a few bubbles **64** is present. However, when the surface area of the one face **52A** is increased, the amount of leached internal liquid **34** increases, and the useable life of the reference electrode **10** will be short.

To resolve this, it is conceivable to reduce the diameter of the liquid junction **52** and fix the liquid junction **52** to the casing **12** using an adhesive agent. However, in such cases, new issues may arise, such as the adhesive agent entering into the liquid junction **52** due to capillary action such that the passageway for the internal liquid **34** is narrowed.

However, in the present embodiment, the head **16** is provided with the overhang portion **58** that hangs out on the one face **52A** side of the liquid junction **52** seated in the seating hole **28**, whereby separation of the liquid junction **52** is prevented. Accordingly, even if a liquid junction **52** with a small outer diameter of 5 mm is employed in the present embodiment, it is possible to extend the life of the reference electrode **10** while preventing the liquid junction **52** from falling out unexpectedly.

A configuration is also conceivable in which the liquid junction **52** is processed into a protruding shape having a small-diameter portion projecting from the casing **12** and a large-diameter portion disposed inside the casing **12** so as to avoid falling-out of the liquid junction **52** and the accumulation of bubbles **64**. However, in such cases, the cost of processing the liquid junction **52** is increased.

In contrast thereto, in the present embodiment, the liquid junction **52** is given a simple, circular column shape, whereby both a fall-out-preventing effect and measurement result stabilization can be simultaneously obtained while reducing costs.

In the present embodiment, the rounded surface region R, which does not project to the one side I of the one face **52A** of the liquid junction **52**, is set on the head surface **16A** of the casing **12** at a part along a circumferential direction around the one face **52A** to form the open portion **62**.

Accordingly, as illustrated in FIG. 5, bubbles **64** discharged through the open portion **62** from the space **60** on the one side I of the liquid junction **52** are able to be smoothly released along the rounded-surface-shaped head surface **16A**.

As a result, when the reference electrode **10** is buried in soil when managing underground pH, even in cases in which the grains of dirt are of large diameter, the one face **52A** of the liquid junction **52** is able to easily make contact with the dirt, enabling the accuracy of pH measurements employing the reference electrode **10** to be improved.

Further, in the present embodiment, the opening **24** is eccentrically disposed with respect to the one face **52A** of the liquid junction **52** seated in the seating hole **28**, enabling the overhang portion **58** to be formed by part of the opening edge **56** of the opening **24**.

Accordingly, configuration is able to be simplified compared with cases in which the overhang portion **58** is provided separately to the casing **12**.

Further, the tube portion **42** of the tank **32** for supplying the internal liquid **34** to the liquid junction **52** abuts the another face **52B** on the another side T of the liquid junction **52** seated in the seating hole **28** of the casing **12**. This enables retreat of the liquid junction **52** from the opening **24** toward the another side T to be suppressed.

As a result, so long as the another face **52B** of the liquid junction **52** is pressed in by the tube portion **42** of the tank **32** until the one face **52A** of the liquid junction **52** abuts the overhang portion **58**, the liquid junction **52** is able to be retained in state held between the overhang portion **58** and the tube portion **42**.

Further, the liquid junction **52** is fixed to the tube portion **42** of the tank **32** by the tubing **54**. Accordingly, a liquid junction **52** with a small diameter of 5 mm or less can be easily seated in the seating hole **28**, and separation of the liquid junction **52** from the tube portion **42** is able to be prevented when the liquid junction **52** is seated.

#### Second Embodiment

FIGS. 6 to 8 illustrate a reference electrode **10** according to a second embodiment. Portions that are the same as, or equivalent to, those in the first embodiment are appended with the same reference numerals and explanation thereof will not be given. Explanation follows for only those portions that differ from the first embodiment.

Namely, a circular-arc-shaped protrusion **70** is formed to the head surface **16A** around the seating hole **28**. An edge **70A** of the protrusion **70** on the apex **20** side of the protrusion **70** is integrally formed to the head surface **16A** (see FIG. 8).

As illustrated in FIGS. 6 and 7, an overhang portion **58** that hangs out toward a hole center **28C** passing through the seating hole **28** is integrally formed to the protrusion **70**, and the opening **24** is provided at the inside of the overhang portion **58**.

As illustrated in FIG. 8, the protrusion **70** is formed with a groove **72** that cuts across the protrusion **70**. As illustrated in FIGS. 6 and 7, the groove **72** divides the overhang portion **58** into a first overhang portion **58B** on the apex **20** side of the overhang portion **58**, and a second overhang portion **58C** on the side of the overhang portion **58** further away from the apex **20**. The first overhang portion **58B** and the second overhang portion **58C** are disposed facing one another.

Further, as illustrated in FIG. 8, a groove bottom face **72A** of the groove **72** formed between the two overhang portions **58B**, **58C** is formed at a position that does not project to the

one side I of the imaginary plane KM making surface contact with the one face 52A of the liquid junction 52 (see, for example, FIGS. 2 and 3). Specifically, the groove bottom face 72A is formed on the imaginary plane KM. A first open portion 62A and a second open portion 62B are thus formed that leave a space 60 on the one side I of the liquid junction 52 that is formed between the two overhang portions 58B, 58C open in lateral directions along the one face 52A.

The present embodiment, configured as described above, is able to achieve similar operation and effects to that of the first embodiment.

Further, in the present embodiment, separation of the liquid junction 52 is able to be prevented by the first overhang portion 58B and the second overhang portion 58C, which are disposed facing one another. Accordingly, an abutting amount T2 (abutting length or surface area) over which the first overhang portion 58B and the second overhang portion 58C abut the liquid junction 52, as illustrated in FIG. 6, is able to be made greater than an abutting amount T1 (abutting length or surface area) over which the single overhang portion 58 abuts the liquid junction 52, as illustrated in FIG. 2. This enables a separation-preventing effect to be increased for the liquid junction 52.

Third Embodiment

FIG. 9 illustrates a reference electrode 10 according to a third embodiment. Portions that are the same as, or equivalent to, those in the first embodiment are appended with the same reference numerals and explanation thereof will not be given. Explanation follows for only those portions that differ from the first embodiment.

In the reference electrode 10 according to the present embodiment, the seating hole 28 penetrates through the head surface 16A, and the opening 24 is formed at a terminal end of the seating hole 28. Four hooks 80 project from an outer circumferential portion of the opening 24. Each of the hooks 80 is provided with a stand-out portion 80A that stands out from the head surface 16A, and with an overhang portion 80B that extends out from the stand-out portion 80A toward the hole center 28C passing through the seating hole 28.

The liquid junction 52 projects from the opening 24 formed by the seating hole 28, and separation of the liquid junction 52 is prevented by the overhang portions 80B of the hooks 80. Thus, when an imaginary plane is envisaged making surface contact with the one face 52A of the liquid junction 52, a region that does not project to the one side I of the imaginary plane is set on the head surface 16A to form the open portion 62.

The present embodiment is also able to achieve similar operation and effects to that of the first embodiment.

Further, in the present embodiment, since the liquid junction 52 projects from the head surface 16A, the internal liquid 34 is also able to be leached from a circumferential face of the liquid junction 52.

Note that in each of the embodiments, although explanation is given using an example in which the opening 24 exposing the liquid junction 52 is provided in a spherical face, there is no limitation thereto. For example, the opening 24 may be provided in a flat face or in an inclined face.

Further, in the present embodiment, although the opening 24 is provided in the spherically formed head surface 16A to form the open portion 62, there is no limitation thereto. For example, a face of a wall surrounding an outer circumferential portion of the one face 52A of the liquid junction 52 may be provided with a through-hole open in a lateral direction S to provide an open portion 62 that leaves the space 60 on the one side I of the liquid junction 52 open in a lateral direction S along the one face 52A.

What is claimed is:

1. A reference electrode, comprising:
  - a casing having an opening formed at a leading end of the casing;
  - a liquid junction provided inside the casing and including a first surface for exuding an internal liquid through the leading end of the casing and a second surface at an opposite side of the liquid junction from the first surface; and
  - in a first direction, in which the first surface and the second surface overlap with each other, the first surface includes a first region that overlaps with the opening and a second region that overlaps with a part of the casing around the opening,
  - wherein in the first region, the first surface is open to an exterior of the casing in a second direction along the first surface, the second direction perpendicular to the first direction.
2. The reference electrode according to claim 1, wherein the casing includes an overhanging portion that overlaps with the second region of the first surface in the first direction and projects toward a side of the first surface.
3. The reference electrode according to claim 1, wherein the opening is formed in a circular shape when viewed from a third direction inclined by a predetermined angle from the first direction.

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