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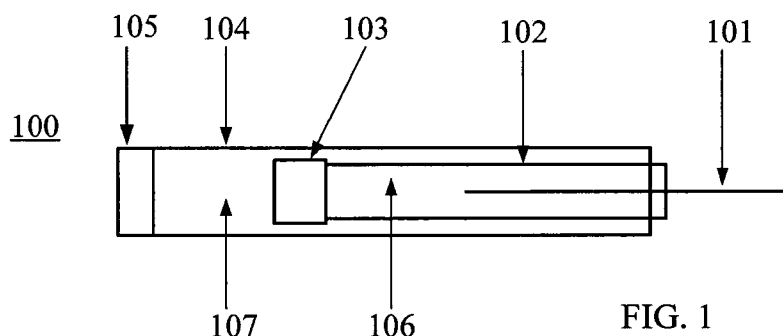


FIG. 1

(57) Abstract: An electrode comprising a first glass tube; an electrically conductive first liquid within the first glass tube defining a first vapor headspace; a silver chloride silver wire passing through the base of the first tube and also being in contact with the first liquid; a second glass tube, the first glass tube passing through the base of the second tube; an electrically conductive second liquid within the second glass tube defining a second vapor headspace; and an interface connecting and providing vapor communication between the first vapor headspace and the second vapor headspace.



ELECTRODE

BACKGROUND

Silver may be reduced to silver nanostructures and, under certain
5 circumstances, specifically to silver nanowires. See, e.g., S. E. Skrabalak; Wiley, BJ; Kim, M; Formo, EV; Xia, Y; *Nano Letters* **2008** 8(7) 2077-81, P-Y Silvert et al., *J. Mater. Chem.* **1997** 7 293-9, and P-Y Silvert et al., *J. Mater. Chem.* **1996** 6 573-7.

Ion selective electrodes are known that operate in mainly in
10 aqueous environments, occasionally in organic media, and generally near room temperature. See, e.g., D. T. Sawyer, A. Sobkowiak, J. L. Roberts, Jr., *Electrochemistry for Chemists*, 2nd Ed., J. Wiley & Sons, New York, 1995. Double junction reference electrodes have been disclosed in US Patent No. 4,401,548.

15 Very little is known about the Ag^+ reduction process or how to control the reaction conditions to optimize a particular morphology: a novel silver ion selective electrode has been designed to operate under high temperatures and in organic solvents to solve this problem. The ion selective electrode may be used to determine the ion concentration at any point during the reaction, enabling the
20 ability to study the chemical details of the reaction process, but in addition may be used in a feedback loop to control the concentration of ions, or the addition point of other components, during the course of the synthesis reaction in order to affect the final properties of the products.

One problem recently discovered with this type of electrode is that
25 at higher temperatures, gases are formed during the reaction that may nucleate to form bubbles in the fine frit separating the bridge solution from the reaction medium, especially if the reaction is run at higher than atmospheric pressure. The bubble disconnects the conductive path and the electrode fails. This invention solves both the atmospheric and above atmospheric gas bubble induced electrical
30 disconnect problems.

SUMMARY

Applicants disclose an ion selective electrode capable of *in situ* long-term monitoring of silver ion concentration at elevated temperatures and pressures in organic media. Such an electrode is useful for monitoring and controlling silver ion concentration during silver nanowire synthesis.

Disclosed is a double junction reference electrode comprising a silver chloride coated silver wire and a liquid filled first glass tube capped by a first frit wherein a first portion of the silver chloride coated silver wire is external to the first glass tube and the internal and external portions of the silver chloride coated silver wire are connected by a portion of silver coated silver wire that passes through the base of the first glass tube opposite the first glass frit; and a liquid filled second glass tube capped by a second frit wherein a first portion of the first glass tube is external to a second glass tube and the second portion of the first glass tube is internal to the second glass tube and the internal and external portions of the first glass tube are connected by a portion of the first glass tube that passes through the base of the second glass tube on the end opposite of the glass frit; and an interface that continuously connects gases above the liquid in the second glass tube to the gases above the liquid in the reaction vessel for the purpose of equilibrating the pressure above the liquids. In some embodiments the first glass tube of the electrode has an outside diameter of about 4 mm and in some embodiments the first glass tube and the first glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the first glass tube and outside the first frit; or, in other embodiments, the first glass frit of the said electrode is fused directly to the glass tube. In some embodiments the first glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3. In some embodiments the second glass tube of the said electrode has an outside diameter of about 10 mm. In other embodiments the second glass tube and the second glass frit of the said electrode are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the second glass tube and outside the second frit; or, in some embodiments, the second glass tube and the second glass frit is fused directly to the glass tube. In some embodiments

the second glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3, and in some embodiments the first glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates, whereas in some embodiments the solution in the first glass tube is a saturated solution of AgCl and KCl in ethylene glycol into which the silver chloride coated silver wire is at least partially submerged. In some embodiments the liquid in the second glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates, whereas in some embodiments, the solution in the second glass tube is a saturated solution of KNO₃ salt in propylene glycol. In some embodiments, the interface connecting the second glass tube to the first comprises a hole in the glass tubing and a concentrically connected fire-polished glass tubing adaptor, whereas in some embodiments, a piece of tubing connects the fire-polished end of the second glass tube to the reaction vessel for the purpose of equalizing pressure between the said reaction vessel and the concentrically connected fire-polished glass tubing adaptor of the said electrode.

Disclosed is a double junction reference electrode comprising a silver chloride coated silver wire and a liquid filled first glass tube capped by a first frit wherein a first portion of the silver chloride coated silver wire is external to the first glass tube and the internal and external portions of the silver chloride coated silver wire are connected by a portion of silver coated silver wire that passes through the base of the first glass tube opposite the first glass frit; and a liquid filled second glass tube capped by a second frit wherein a first portion of the first glass tube is external to a second glass tube and the second portion of the first glass tube is internal to the glass tube and the internal and external portions of the first glass tube are connected by a portion of the first glass tube that passes through the base of the second glass tube on the end opposite of the glass frit; and a means for modifying the surface tension of the liquid in the second tube and the inner surface of the second tube. In some embodiments first glass tube of the said electrode has an outside diameter of about 4 mm, whereas in some embodiments, the first glass tube and the first glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the first glass tube and

outside the first frit; whereas in some embodiments the first glass tube and the first glass frit is fused directly to the glass tube whereas in yet other embodiments the first glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3. In some embodiments the second glass tube has an outside diameter of about 10 mm,

5 whereas in other embodiments the second glass tube and the second glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the second glass tube and outside the second frit; or, in other embodiments, second glass tube and the second glass frit is fused directly to the glass tube. In some embodiments the second glass frit is a VitraPOR frit

10 fabricated from borosilicate glass 3.3, and in some embodiments, the liquid in the first glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates. In some embodiments the solution in the first glass tube is a saturated solution of AgCl and KCl in ethylene glycol into which the silver chloride coated silver wire is at least

15 partially submerged. In some embodiments the liquid in the second glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature and pressure at which the electrode operates, whereas in some embodiments, the solution in the second glass tube is a saturated solution of KNO₃ salt in propylene glycol. In some embodiments, the inner surface of the second

20 glass tube comprises at least one surface tension modifier in the form of silyl groups, organo-fluorine groups or other suitable chemical modifiers used to alter the surface tension between the inner glass surface of the second glass tube and the liquid in the second glass tube. In some embodiments, the inner surface of the second tube comprises a nanotextured (super-hydrophobic or super-omniphobic)

25 surface applied to minimize the surface tension between the inner walls of the second s glass tube and the liquid in the second glass tube.

Disclosed is a double junction reference electrode comprising a silver chloride coated silver wire and a liquid filled first glass tube capped by a first frit wherein a first portion of the silver chloride coated silver wire is external

30 to the first glass tube and the internal and external portions of the silver chloride coated silver wire are connected by a portion of silver coated silver wire that passes through the base of the first glass tube opposite the first glass frit; and a

liquid filled second glass tube capped by a second frit wherein a first portion of the first glass tube is external to a second glass tube and the second portion of the first glass tube is internal to the glass tube and the internal and external portions of the first glass tube are connected by a portion of the first glass tube that passes

5 through the base of the second glass tube on the end opposite of the glass frit; and a means for modifying the surface tension of the liquid in the second tube and the inner surface of the second tube; and an interface that continuously connects gases above the liquid in the second glass tube to the gases above the liquid in the reaction vessel for the purpose of equilibrating the pressure above the liquids. In

10 some embodiments the said electrode comprises a first glass tube has an outside diameter of about 4 mm, whereas in some embodiments, the first glass tube and the first glass frit of the said electrodes are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the first glass tube and outside the first frit; or, in some embodiments, first glass tube and the first glass

15 frit of the said electrode is fused directly to the glass tube. In some embodiments, the first glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3. In some embodiments the second glass tube has an outside diameter of about 10 mm. In some embodiments, the second glass tube and the second glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted

20 outside of the second glass tube and outside the second frit; or, in some embodiments, the second glass tube and the second glass frit is fused directly to the glass tube. In some embodiments, the second glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3. In some embodiments, the first glass tube is a solvent and salt combination capable of providing electrical conductivity at

25 the temperature at which the electrode operates. In some embodiments, the solution in the first glass tube is a saturated solution of AgCl and KCl in ethylene glycol into which the silver chloride coated silver wire is at least partially submerged. In some embodiments, the liquid in the second glass tube is a solvent and salt combination capable of providing electrical conductivity at the

30 temperature at which the electrode operates, and in some embodiments the solution in the second glass tube is a saturated solution of KNO₃ salt in propylene glycol. In some embodiments, the inner surface of the second glass tube of the

said electrode comprises at least one surface tension modifier in the form of silyl groups, organo-fluorine groups, or other suitable chemical modifiers to modify the surface tension between the inner glass surface of the second glass tube and the liquid comprised in the second glass tube, whereas in some embodiments, the
5 inner surface of the second tube comprises at least one nanotextured (super-hydrophobic or super-omniphobic) surface applied to minimize the surface tension between the inner walls of the second glass tube and the liquid in the second glass tube. In some embodiments, the interface connecting the second glass tube to the first comprises a hole in the glass tubing and a concentrically
10 connected fire-polished glass tubing adaptor, and in some embodiments a piece of tubing connects the fire-polished end of the second glass tube to the reaction vessel for the purpose of equalizing pressure between the said reaction vessel and the concentrically connected fire-polished glass tubing adaptor.

Disclosed is a double junction reference electrode comprising a first
15 glass tube capped by a first frit and having a first base opposite the first frit; an electrically conductive first liquid within the first glass tube defining a first vapor headspace between the first liquid and the first frit; a silver chloride silver wire passing through the first base and defining a first portion of the silver chloride silver wire being external to the first glass tube and a second portion of the silver
20 chloride silver wire being internal to the first glass tube, the second portion of the silver chloride silver wire also being in contact with the first liquid; a second glass tube capped by a second frit, having a second base opposite the second frit, and having an inner surface, the first glass tube passing through the second base and defining a first portion of the first glass tube being external to the second glass
25 tube and a second portion of the first glass tube being internal to the second glass tube, the first and second portions of the first glass tube being in fluid communication with each other; an electrically conductive second liquid within the second glass tube defining a second vapor headspace between the second liquid and the second frit; and an interface connecting and providing vapor
30 communication between the first vapor headspace and the second vapor headspace. In some such embodiments, the electrically conductive first liquid is a saturated solution of AgCl and KCl in ethylene glycol. In some of the above

embodiments, the electrically conductive second liquid is a saturated solution of KNO_3 in propylene glycol. In some of the above embodiments, the first glass frit is fabricated from borosilicate glass 3.3. In some of the above embodiments, the second glass frit is fabricated from borosilicate glass 3.3. In some of the above
5 embodiments, the inner surface of the second glass tube comprises at least one surface tension modifying compound comprising silyl groups or organo-fluorine groups. In some of the above embodiments, the inner surface of the second glass tube is nanotextured, such as, for example, a superhydrophobic or omniphobic surface.

10 Disclosed is a system comprising the double junction reference electrode according to any of the above embodiments and a reaction vessel, the reaction vessel containing a reaction mixture defining a third vapor headspace above the reaction mixture, where the third vapor headspace is in vapor communication with first vapor headspace and the second vapor headspace of the
15 double junction reference electrode. Such a reaction mixture comprises a liquid and may also comprise solids, such as, for example, silver nanowires. In some such systems, the third vapor headspace is in vapor communication with the adapter of the double junction reference electrode.

20 DESCRIPTION OF FIGURES

FIG. 1 depicts the double junction reference electrode of Example 1.

FIG. 2 depicts the voltage (mV) between a working electrode and the double junction reference electrode of FIG. 1, as a function of time (min),
25 according to the procedure of Example 1.

FIG. 3 depicts the double junction reference electrode of Example 2, including bridge solution glass tube portion (200-203), pressure equalizing adaptor (204), and adaptor (205) for the bridge solution tube.

FIG. 4 depicts the double junction reference electrode of FIG. 3
30 and pressure relief system, incorporated with reaction vessel.

FIG. 5 depicts the voltage (mV) between a working electrode and the double junction reference electrode of FIG. 4, as a function of time (min),

according to the procedure of Example 2.

DESCRIPTION

5 All publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference.

U.S. Provisional Patent Application No. 62/170,164, entitled “ELECTRODE,” filed on June 3, 2015, is incorporated by reference in its entirety.

10 As used herein, “a” or “an” component refers to “at least one” or “one or more” of that component.

Materials and Equipment

The LabVIEW® programming environment is available from National Instruments, 11500 Mopac Expwy, Austin Texas, 78759-3504, USA.

15 The ACCUMET® AP61 portable voltmeter is available from Fisher Scientific 81 Wyman Street Waltham, MA 02451 Phone Number: (781) 622-1000.

The SCOTCH-BRITE brand scouring pad is available from 3M Corporation, 3M Center, St. Paul, MN 55144-1000.

20 TEFLON® brand polytetrafluoroethylene (PTFE) is available from DuPont Co, 1007 North Market Street Wilmington DE 19898.

KCl is potassium chloride.

AgCl is silver chloride.

25 VYCOR® brand high silica, high temperature glass is available from Corning, Inc, Dow Corning Corporation, Corporate Center, PO Box 994 Midland, Michigan 48686-0994 USA.

PG is propylene glycol.

AgNO₃ is silver nitrate.

HNO₃ is nitric acid.

30 CHEMGLASS® 24/40 adapter has a serrated hose connection for vacuum or for the introduction of gases. The #7 CHEM-THREAD at the top is for a vacuum tight seal of plain stem thermometers or any other tube having an

O.D. between 4 and 7mm. Serrated hose connection has an O.D. of 10mm at the largest serration. It is supplied complete with a compression cap and VITON o-ring. It is available from Chemglass Life Sciences, 3800 N. Mill Road, Vineland, NJ 08360.

5 Borosilicate glass is a type of glass with silica and boron trioxide as the main glass-forming constituents. Usually it comprises at least 5% boric oxide. The boric oxide makes the glass resistant to extreme temperatures, and also improves its resistance to chemical corrosion. Borosilicate 3.3 glass has coefficient of mean linear thermal expansion α (20 °C; 300 °C) of $3.3 \times 10^{-6} \text{ K}^{-1}$
10 according to DIN ISO 7991. Borosilicate glass is sold under such trade names as SIMAX®, BORCAM®, BOROSIL®, SUPRAX, KIMAX®, HEATEX®, PYREX®, ENDURAL®, SCHOTT®, and REFMEX.

Superhydrophobic and omniphobic surfaces are surfaces engineered to repel both polar and nonpolar liquids simultaneously. These surfaces
15 ideally display water contact angles greater than 150°, and in addition display low contact angle hysteresis which allows for fully-equilibrated, composite interfaces with drops of liquids such as alkanes or alcohols that possess significantly lower surface tension than water. These surfaces have been known to repel, for example, pentane which has a surface tension of 15.7 mN/m.

20

EXEMPLARY EMBODIMENTS

U.S. Provisional Patent Application No. 62/170,164, entitled “ELECTRODE,” filed on June 3, 2015, which is incorporated by reference in its entirety, disclosed the following 41 exemplary non-limiting embodiments:

25 A. A double junction reference electrode comprising a silver chloride coated silver wire and a liquid filled first glass tube capped by a first frit wherein a first portion of the silver chloride coated silver wire is external to the first glass tube and the internal and external portions of the silver chloride coated silver wire are connected by a portion of silver coated silver wire that passes through the base of
30 the first glass tube opposite the first glass frit; and

a liquid filled second glass tube capped by a second frit wherein a first portion of the first glass tube is external to a second glass tube and the second

portion of the first glass tube is internal to the second glass tube and the internal and external portions of the first glass tube are connected by a portion of the first glass tube that passes through the base of the second glass tube on the end opposite of the glass frit; and

- 5 an interface that continuously connects gases above the liquid in the second glass tube to the gases above the liquid in the reaction vessel for the purpose of equilibrating the pressure above the liquids.

B. The electrode of embodiment A wherein the first glass tube has an outside diameter of about 4 mm

- 10 C. The electrode of embodiment A wherein the first glass tube and the first glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the first glass tube and outside the first frit; or,

 the electrode of embodiment A wherein the first glass tube and the first glass frit is fused directly to the glass tube.

- 15 D. The electrode of embodiment A wherein the first glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3.

E. The electrode of embodiment A wherein the second glass tube has an outside diameter of about 10 mm.

- 20 F. The electrode of embodiment A wherein the second glass tube and the second glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the second glass tube and outside the second frit; or,

 the electrode of embodiment A wherein the second glass tube and the second glass frit is fused directly to the glass tube.

- 25 G. The electrode of embodiment A wherein the second glass frit is a VitraPOR® frit fabricated from borosilicate glass 3.3.

H. The electrode of embodiment A wherein the liquid in the first glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates.

- 30 J. The electrode of embodiment H wherein the solution in the first glass tube is a saturated solution of AgCl and KCl in ethylene glycol into which the silver chloride coated silver wire is at least partially submerged.

K. The electrode of embodiment A wherein the liquid in the second glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates.

5 L. The electrode of embodiment K wherein the solution in the second glass tube is a saturated solution of KNO_3 salt in propylene glycol

M. The electrode of embodiment A wherein the interface connecting the second glass tube to the first comprises a hole in the glass tubing and a concentrically connected fire-polished glass tubing adaptor.

10 N. The electrode of embodiment M wherein a piece of tubing connects the fire-polished end of the second glass tube to the reaction vessel for the purpose of equalizing pressure between the said reaction vessel and the concentrically connected fire-polished glass tubing adaptor.

15 P. A double junction reference electrode comprising a silver chloride coated silver wire and a liquid filled first glass tube capped by a first frit wherein a first portion of the silver chloride coated silver wire is external to the first glass tube and the internal and external portions of the silver chloride coated silver wire are connected by a portion of silver coated silver wire that passes through the base of the first glass tube opposite the first glass frit; and

20 a liquid filled second glass tube capped by a second frit wherein a first portion of the first glass tube is external to a second glass tube and the second portion of the first glass tube is internal to the glass tube and the internal and external portions of the first glass tube are connected by a portion of the first glass tube that passes through the base of the second glass tube on the end opposite of the glass frit; and

25 a means for modifying the surface tension of the liquid in the second tube and the inner surface of the second tube.

Q. The electrode of embodiment P wherein the first glass tube has an outside diameter of about 4 mm.

30 R. The electrode of embodiment P wherein the first glass tube and the first glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the first glass tube and outside the first frit; or,

the electrode of embodiment P wherein the first glass tube 102 and

the first glass frit is fused directly to the glass tube.

S. The electrode of embodiment P wherein the first glass frit is a VitraPOR frit fabricated from borosilicate glass 3.3.

5 T. The electrode of embodiment P wherein the second glass tube has an outside diameter of about 10 mm.

U. The electrode of embodiment P wherein the second glass tube and the second glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the second glass tube and outside the second frit; or,

10 the electrode of embodiment P wherein the second glass tube and the second glass frit is fused directly to the glass tube.

V. The electrode of embodiment P wherein the second glass frit is a VitraPOR frit fabricated from borosilicate glass 3.3.

15 W. The electrode of embodiment P wherein the liquid in the first glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates

X. The electrode of embodiment W wherein the solution in the first glass tube is a saturated solution of AgCl and KCl in ethylene glycol into which the silver chloride coated silver wire is at least partially submerged

20 Y. The electrode of embodiment P wherein the liquid in the second glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature and pressure at which the electrode operates.

Z. The electrode of embodiment Y wherein the solution in the second glass tube is a saturated solution of KNO₃ salt in propylene glycol.

25 AA. The electrode of embodiment P wherein the inner surface of the second glass tube comprises at least one surface tension modifier in the form of silyl groups, organo-fluorine groups or other suitable chemical modifiers used to alter the surface tension between the inner glass surface of the second glass tube and the liquid in the second glass tube

30 AB. The electrode of embodiment Q wherein the inner surface of the second tube comprises a nanotextured (super-hydrophobic or super-omniphobic) surface applied to minimize the surface tension between the inner walls of the second

glass tube and the liquid in the second glass tube.

AC. A double junction reference electrode comprising a silver chloride coated silver wire and a liquid filled first glass tube capped by a first frit wherein a first portion of the silver chloride coated silver wire is external to the first glass tube
5 and the internal and external portions of the silver chloride coated silver wire are connected by a portion of silver coated silver wire that passes through the base of the first glass tube opposite the first glass frit; and

a liquid filled second glass tube capped by a second frit wherein a first portion of the first glass tube is external to a second glass tube and the second
10 portion of the first glass tube is internal to the glass tube and the internal and external portions of the first glass tube are connected by a portion of the first glass tube that passes through the base of the second glass tube on the end opposite of the glass frit; and

a means for modifying the surface tension of the liquid in the
15 second tube and the inner surface of the second tube; and

an interface that continuously connects gases above the liquid in the second glass tube to the gases above the liquid in the reaction vessel for the purpose of equilibrating the pressure above the liquids.

AD. The electrode of embodiment AC wherein the first glass tube has an outside
20 diameter of about 4 mm.

AE. The electrode of embodiment AC wherein the first glass tube and the first glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the first glass tube and outside the first frit; or,
the electrode of embodiment AC wherein the first glass tube and
25 the first glass frit is fused directly to the glass tube.

AF. The electrode of embodiment AC wherein the first glass frit is a VitraPOR frit fabricated from borosilicate glass 3.3.

AG. The electrode of embodiment AC wherein the second glass tube has an outside diameter of about 10 mm.

AH. The electrode of embodiment AC wherein the second glass tube and the second glass frit are heat sealed to each other via use of a heat treated intermediate TEFLON® tube fitted outside of the second glass tube and outside the second frit;

or,

the electrode of embodiment AC wherein the second glass tube and the second glass frit is fused directly to the glass tube.

AJ. The electrode of embodiment AC wherein the second glass frit is a

5 VitraPOR® frit fabricated from borosilicate glass 3.3.

AK. The electrode of embodiment AC wherein the liquid in the first glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates

AL. The electrode of embodiment AK wherein the solution in the first glass tube
10 is a saturated solution of AgCl and KCl in ethylene glycol into which the silver chloride coated silver wire is at least partially submerged.

AM. The electrode of embodiment AC wherein the liquid in the second glass tube is a solvent and salt combination capable of providing electrical conductivity at the temperature at which the electrode operates.

15 AN. The electrode of embodiment AM wherein the solution in the second glass tube is a saturated solution of KNO₃ salt in propylene glycol.

AP. The electrode of embodiment AC wherein the inner surface of the second glass tube comprises at least one surface tension modifier in the form of silyl groups, organo-fluorine groups other suitable chemical modifier to modify the
20 surface tension between the inner glass surface of the second glass tube and the liquid comprised in the second glass tube.

AQ. The electrode of embodiment AC wherein the inner surface of the second tube comprises at least one nanotextured (super-hydrophobic or super-omniphobic) surface applied to minimize the surface tension between the inner
25 walls of the second second glass tube and the liquid in the second glass tube.

AR. The electrode of embodiment AC wherein the interface connecting the second glass tube to the first comprises a hole in the glass tubing and a concentrically connected fire-polished glass tubing adaptor.

AS. The electrode of embodiment AR wherein a piece of tubing connects the fire-
30 polished end of the second glass tube to the reaction vessel for the purpose of equalizing pressure between the said reaction vessel and the concentrically connected fire-polished glass tubing adaptor.

EXAMPLES

Ion concentrations in reactions run at atmospheric and above atmospheric pressure can be monitored using an ion selective electrode that incorporates either or both a pressure equalizing tube and a surface tension modifier. In Example 1, an Ag^+ ion sensitive electrode system capable of operating without error at atmospheric pressure is described. In Example 2, a modification to electrode which allows the electrode to function at reaction pressures above atmospheric pressure is described. In Example 3, a surface tension modifier is described which assists with the disposal of any gas bubble forming within the electrode at temperatures above room temperature and pressures above atmospheric pressure.

Example 1

A working electrode was constructed by cleaning a 7.0 mm diameter 99.99% pure solid silver rod with a mild SCOTCH-BRITE pad prior to each use. A double junction reference electrode (100) was constructed as shown in Fig. 1. The reference electrode employed a silver chloride coated wire (101) immersed in a $\text{KCl}_{\text{saturated}}\text{-AgCl}_{\text{saturated}}/\text{Ag}/\text{AgCl}$ ethylene glycol solution (106) enclosed in a 4 mm glass tube (102) capped with a 4 mm VYCOR® porous glass frit (103) (G0300, Princeton Applied Research), heat sealed with a TEFLON® sleeve, which was inserted into a saturated KNO_3 propylene glycol bridge solution (107) in a 10 mm outside diameter glass tube (104) fused to a 4 mm glass tube capped (105) with a 4 mm VYCOR® porous glass frit sealed with a TEFLON® sleeve.

The working electrode and the glass frit end of the double junction reference electrode were immersed in a flask containing 400 mL of propylene glycol which was heated to 150 °C. To the propylene glycol was added 0.57 mL of a 1.0 M solution of AgNO_3 in propylene glycol. The voltage between the working electrode and the double junction reference electrode were monitored as a function of time. Fig. 2 shows the decrease in voltage measured over time. The

voltage measured is a function of the silver ion concentration, which decreased as Ag^+ ions were reduced to silver metal. Once the voltage readings stabilized, an additional 0.57 mL of the 1.0 M solution in propylene glycol was injected into the flask to assess reproducibility. As shown in Fig. 2, the voltage measured

5 increased shortly after the injection, then again decayed with time, as the added Ag^+ ions were reduced to silver metal.

Example 2

This example illustrates an improvement to the electrode described

10 in Example 1 that allows the electrode to function under reaction conditions in which the pressure is greater than atmospheric pressure. The improvement involves refinement of the double junction electrode (100) with an improved design (200), shown in Fig. 3, in which the fundamental modification was the replacement of the outer glass tube (104) which holds the bridge solution with a

15 new design (202) that maintains equal pressure between the reaction vessel and the bridge solution within the tube. With the addition of the pressure equalizing system, the buildup of bubbles in the propylene glycol bridge solution (107) was minimal or non-existent.

The improved double junction electrode (200) was incorporated

20 into the reaction vessel as shown in Fig. 4. The outer glass tube (202) was inserted into the reaction vessel through the pressure equalizing adaptor for the bridge solution (205) and sealed with a CHEMGLASS® fitting (204). The 4 mm glass tube (102) that comprises the reference electrode was placed through the outer glass tube and sealed with a threaded fitting (203). Tubing (206) connected

25 the reaction vessel (207) to the outer glass tube (202).

The electrode defined in Example 1 and modified as described in this example was used to monitor the Ag^+ ion concentration at 150° C in propylene glycol in the following experiment: at 0.25 mL/min, 1.0 M AgNO_3 and 0.25 M NaNO_2 in propylene glycol are added to a mixture of

30 polyvinylpyrrolidone, NH_4Cl , and NH_4Br in propylene glycol at 150°C. The Ag^+ ion concentration was monitored using the Ag^+ selective electrode. The voltage on the electrode is a function of the silver ion concentration. Voltage (mV) is

plotted as a function of time (min) in Fig. 5. The black dashed line and the solid black line comprise the electrode response from comparison examples. The solid portion shows the effect of a gas bubble that electrically disconnects the electrode response and the dashed is the actual response when there is no gas bubble disconnection. The dotted black line is the response from the invention electrode showing no bubble induced disconnects.

The output of this combination is a voltage reading that is functionally related to the free silver ion concentration by the Nernst equation adjusted for the temperature at which readings are taken. Direct voltage readings are taken from a standard meter such as an ACCUMET® AP61, or fed into automated data collection software such as LabView®.

Example 3

A surface tension modifier applied to the inner surface of the bridge solution tube, which allows more facile release of any gas bubble that is forming, can be applied to the device described in Example 1 or Example 2. The surface tension modifier can be chemical, such as from treatment to add silyl groups, organo-fluorine groups, or other suitable chemical modifiers, to the glass surface, or a mechanical modification of the glass surface, such as providing nanotextured (super-hydrophobic or super-omniphobic) surfaces.

Many organic solvents may be used in this construction, the main requirements are that the solvents dissolve a suitable salt for conductivity and having a boiling point at or above the temperature at which the electrode is desired to operate.

The output of this combination is a voltage reading that is functionally related to the free silver ion concentration by the Nernst equation adjusted for the temperature at which readings are taken. Direct voltage readings are taken from a standard meter such as an ACCUMET® AP61, or fed into an automated data collection software such as LabView®.

Surface tension modification by silylation: the bridge solution glass tube (this example uses the pressure equalizing version shown above) was cleaned in 35% HNO₃, thoroughly rinsed and dried. Next, the tube was inserted

into a 5% solution of diethyldichlorosilane in hexane for about 10 minutes,
drained and allowed to air dry. The exterior of the tube to be connected to the frit
via thermally shrinking a TEFLON® tube was cleaned of the silane with 600 grit
sandpaper. The ion specific reference electrode was then constructed as described
5 in Examples 1 and 2.

The invention has been described in detail with reference to
specific embodiments, but it will be understood that variations and modifications
can be effected within the spirit and scope of the invention. The presently
disclosed embodiments are therefore considered in all respects to be illustrative
10 and not restrictive. The scope of the invention is indicated by the attached claims,
and all changes that come within the meaning and range of equivalents thereof are
intended to be embraced therein.

CLAIMS:

1. A double junction reference electrode comprising:
 - a first glass tube capped by a first frit and having a first base opposite the first frit;
 - an electrically conductive first liquid within the first glass tube defining a first vapor headspace between the first liquid and the first frit;
 - a silver chloride silver wire passing through the first base and defining a first portion of the silver chloride silver wire being external to the first glass tube and a second portion of the silver chloride silver wire being internal to the first glass tube, the second portion of the silver chloride silver wire also being in contact with the first liquid;
 - a second glass tube capped by a second frit, having a second base opposite the second frit, and having an inner surface, the first glass tube passing through the second base and defining a first portion of the first glass tube being external to the second glass tube and a second portion of the first glass tube being internal to the second glass tube, the first and second portions of the first glass tube being in fluid communication with each other;
 - an electrically conductive second liquid within the second glass tube defining a second vapor headspace between the second liquid and the second frit; and
 - an interface connecting and providing vapor communication between the first vapor headspace and the second vapor headspace.
2. The double junction reference electrode according to claim 1, wherein the electrically conductive first liquid is a saturated solution of AgCl and KCl in ethylene glycol.
3. The double junction reference electrode according to either of claims 1 or 2, wherein the electrically conductive second liquid is a saturated solution of KNO₃ in propylene glycol.

4. The double junction reference electrode according to any of claims 1-3, wherein the first glass frit is fabricated from borosilicate glass 3.3.

5. The double junction reference electrode according to any of claims 1-4, wherein the second glass frit is fabricated from borosilicate glass 3.3.

6. The double junction reference electrode according to any of claims 1-5, wherein the inner surface of the second glass tube comprises at least one surface tension modifying compound comprising silyl groups or organo-fluorine groups.

7. The double junction reference electrode according to any of claims 1-6, wherein the inner surface of the second glass tube is nanotextured.

8. A system comprising the double junction reference electrode according to any of claims 1-7 and a reaction vessel,
the reaction vessel containing a reaction mixture defining a third vapor headspace above the reaction mixture,
wherein the third vapor headspace is in vapor communication with first vapor headspace and the second vapor headspace.

9. The system according to claim 8, wherein the third vapor headspace is in vapor communication with the adapter.

1/4

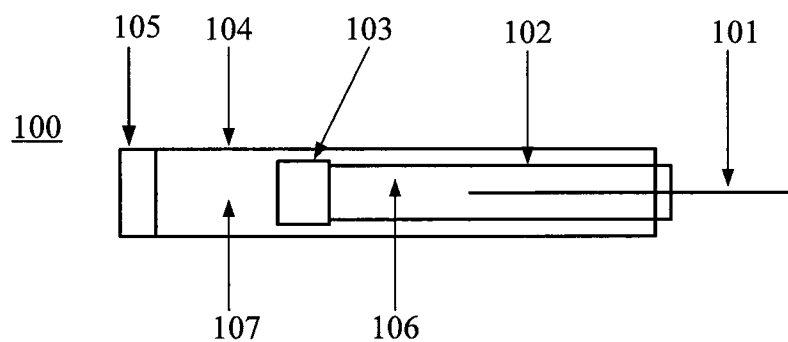


FIG. 1

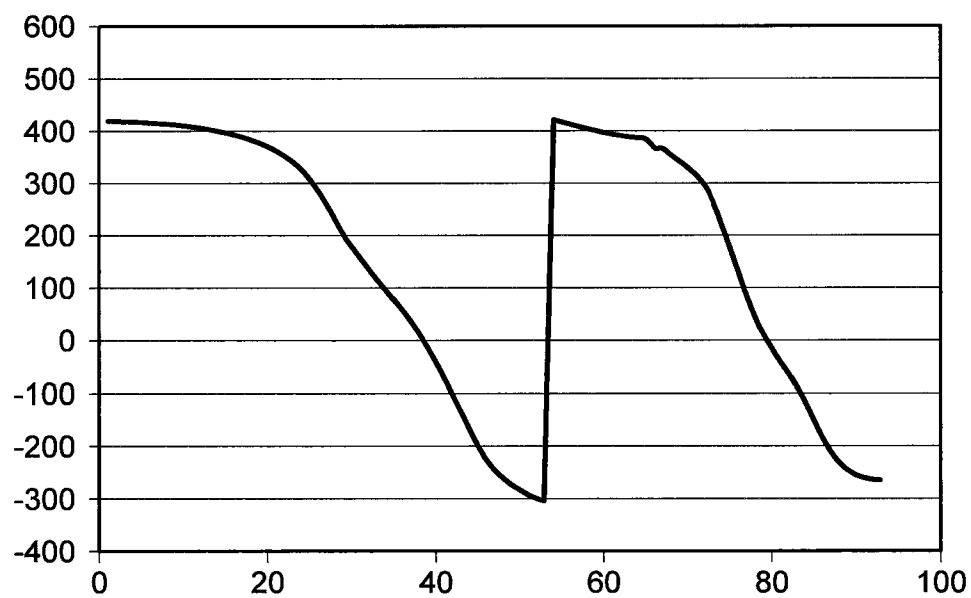


FIG. 2

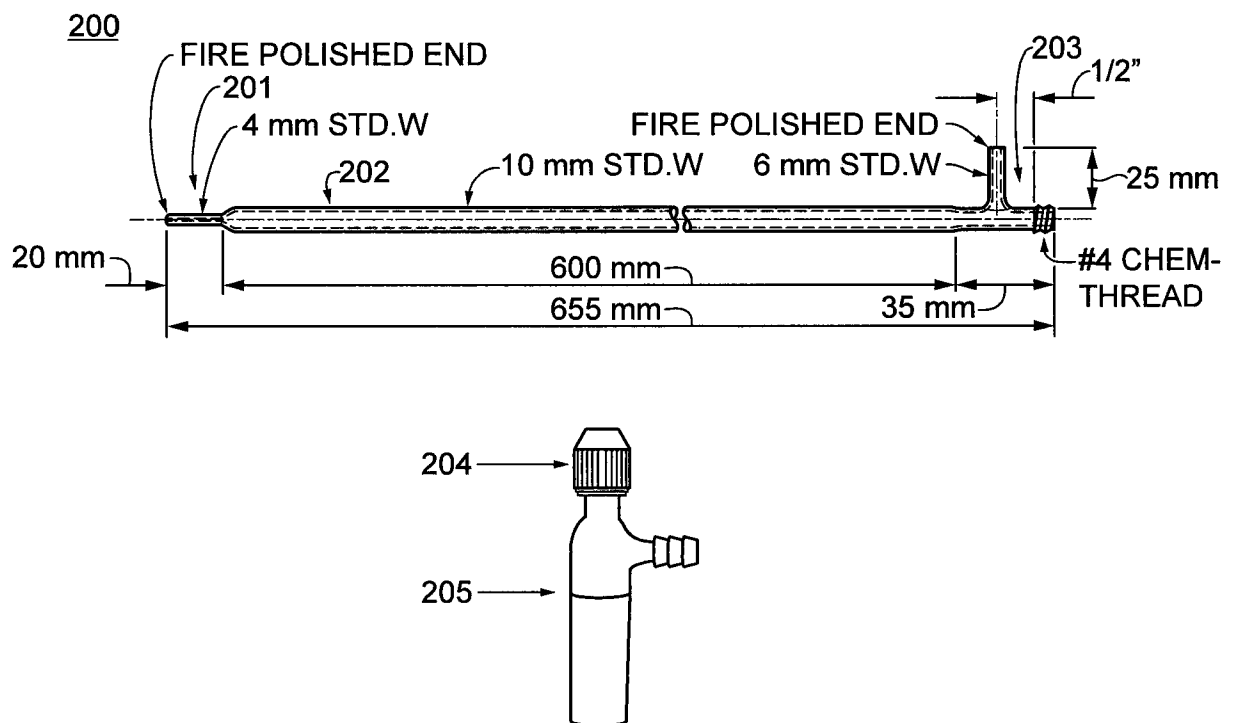


FIG. 3

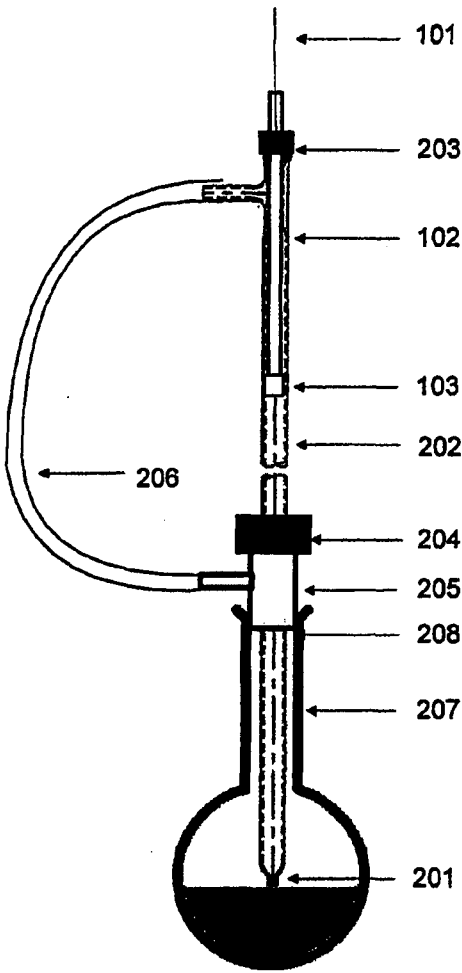


FIG. 4

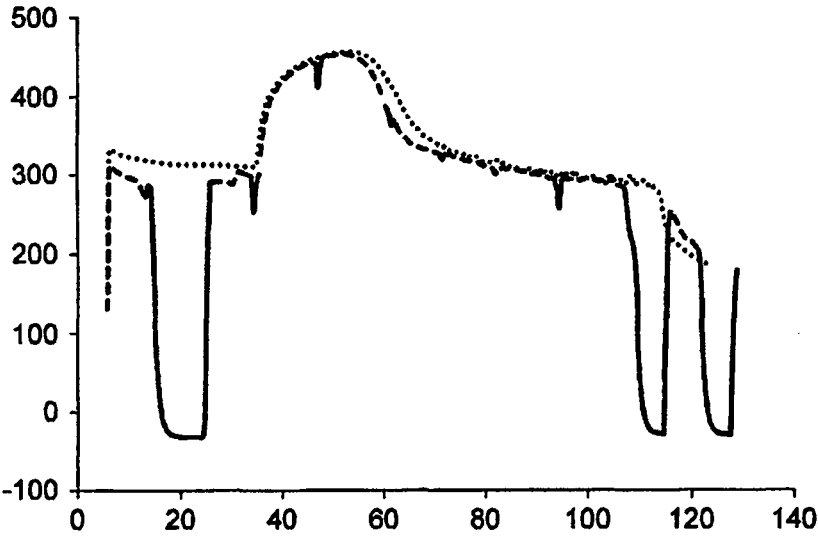


FIG. 5

A. CLASSIFICATION OF SUBJECT MATTER**G01N 27/407(2006.01)I, G01N 27/414(2006.01)I, G01N 1/22(2006.01)I**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G01N 27/407; G01N 27/40; G01N 27/00; H01M 4/66; G01N 27/30; H01L 29/66; C08J 9/00; G01N 27/414; G01N 1/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: double junction, reference electrode, chloride, ethylene glycol, KCL, AgCl, KNO, borosilicate, glass frit, vapor, space, wire, ion selective, interface, conductive, liquid and reaction vessel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002-0065332 A1 (CHOI et al.) 30 May 2002	1-3, 8-9
Y	See paragraphs [0005], [0018], [0086]-[0087], [0100]-[0104] and figures 1-3b.	4-7
Y	US 2011-0227558 A1 (MANNION et al.) 22 September 2011	4-7
	See paragraphs [0051], [0435], [0705].	
A	US 2006-0141362 A1 (NANNO et al.) 29 June 2006	1-9
	See paragraphs [0012]-[0024], [0041], [0066] and figure 1.	
A	US 2014-0102897 A1 (NISSAN NORTH AMERICA, INC.) 17 April 2014	1-9
	See paragraphs [0003]-[0004], [0020]-[0021] and figure 1.	
A	WO 2014-204293 A1 (MIMOS BERHAD) 24 December 2014	1-9
	See paragraphs [9]-[13] and figure 1.	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

27 September 2016 (27.09.2016)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/035369

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US 2014-0102897 A1	17/04/2014	None	
WO 2014-204293 A1	24/12/2014	None	