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— *of inventorship (Rule 4.17(iv))*

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(54) Title: REFERENCE ELECTRODE

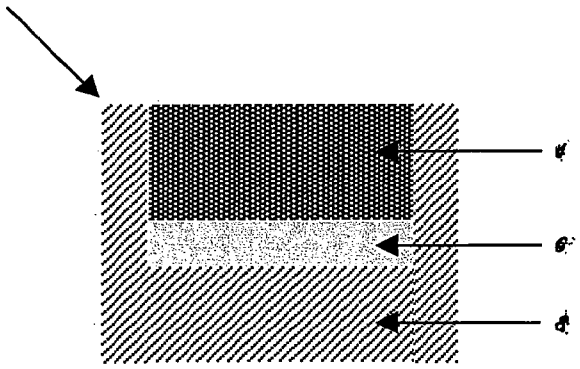


Figure 1

(57) Abstract: The present invention relates to a solid-state reference electrode that can be used to conduct in-situ measurement in harsh environmental conditions. The solid-state reference electrode comprises of a silver-silver halide electrode, halide salt, and low impedance organic binder within a casing.

REFERENCE ELECTRODE

Field of invention

This present invention relates to a reference electrode, and more specifically, to a solid-state reference electrode.

Background of the invention

As environmental conditions worsen everyday due to the ever-changing climate and increased human activities, there is an increasing need to utilize various types of equipments/apparatuses to monitor the quality of the environment.

One of these monitoring apparatuses is the reference electrode. A reference electrode has been commonly used along with a working electrode or a sensor to monitor the quality of the natural water bodies. This is to ensure that the concentration of the contaminants do not exceed the permitted levels that may sometimes cause irreversible damage to the environment.

In potentiometric measurement, the reference electrode is equally important as the working electrode. This is because both electrodes contribute to the accuracy of the measured data.

However, due to the harsh environmental conditions, the reference electrode will wear out through repeated use in a short period of time, and thereby affect the reading of the concentration of contaminants in the natural water bodies. Therefore, there arises a need to maintain and calibrate the reference electrode regularly. This will incur high maintenance and calibration costs, and consume time and manpower in the long run. Furthermore, the reference electrode may be utilized in inaccessible areas making routine

maintenance and calibration checks of the reference electrode more difficult to conduct.

EP 0 682 247 A1 relates to a reference electrode. It is generally suited for use in a water quality monitoring apparatus. Generally, the reference electrode comprises of a substrate of insulating material, a silver layer supported on the substrate, a terminal region of the electrode comprising one portion of the silver layer, a silver halide layer which is arranged to overlay another portion of the silver layer, an insulation layer (epoxy binder) which is arranged to mask a surface of the silver layer between the said one portion and the said silver halide layer, and a contact region of the said electrode defined by a layer comprising a salt of the halide which overlays the said silver halide layer.

However, EP 0 682 247 A1 merely mentioned the use of reference electrode to measure or monitor the quality or character of liquid, i.e. water and does not disclose the use of the reference electrode to monitor water quality in harsh environmental conditions.

Thus, a need exists for an improved reference electrode with the capability to withstand harsh environmental conditions, i.e. extreme pH, temperatures, pressures, polluted rivers, treatment ponds, sewage etc, to conduct in-situ measurement accurately and eliminate or reduce the need to maintain and calibrate the reference electrode regularly.

Summary of the invention

Accordingly, an object of the present invention is to provide a solid-state reference electrode that can be used to conduct in-situ measurement in harsh environmental conditions. The solid-state reference electrode comprises of a silver-silver halide electrode, halide salt, and low impedance organic binder within a casing. The present invention also teaches the method of producing the

solid-state reference electrode of the present invention. The solid-state reference electrode of the present invention may form a part of an integrated wireless chemical sensor system.

Brief description of the drawings

Figure 1 is a schematic diagram of the solid-state reference electrode according to the present invention.

Figure 2 shows the responses of nitrate and potassium ion-selective electrode (ISE) chemical sensors with a solid-state reference electrode (Solid 2).

Detailed description of the invention

Referring to Figure 1, a solid-state reference electrode [2] in accordance with the invention, comprises of a tubular casing [8], which is made of Teflon or other similar coating. A wire [6] serves as an electrical conductor. The said wire [6] is made of silver or platinum and it is coiled at the bottom of the casing [8]. It passes through a hole at the bottom of the casing [8] for electrical contact. The wire [6] is secured in its position by using epoxy glue. A circular shaped silver foil acts as a support to the wire [6], wherein the said foil is mechanically pressed onto the silver wire [6].

Equal weight ratio of silver nanoparticles, silver halide crystals and halide salts are homogenously combined. Then, a low impedance organic binder is added to the mixture to glue all the solid electrolyte materials together and provide low impedance current path for the electrical signal. A thick paste of silver-silver halide-halide salts-binder composition [4] is formed. The tubular casing [8] containing the wire [6] and silver foil is filled with the paste. The paste [4] is then pressed mechanically at high pressure and cured in an oven under high temperature for about 1 to 10 hours.

The following example serves to illustrate the present invention, but should not be construed as in any way limiting its scope.

Example 1

This example illustrates a method for producing the solid-state reference electrode of the present invention.

The tubular Teflon casing was constructed by drilling holes into a Teflon rod, forming a diameter of 3 mm and height of 4 mm. The casing's wall and base are 1.5 mm thick. A smaller hole was drilled at the wall just above the floor of the Teflon rod to allow a 0.5 mm diameter silver wire to pass through. The wire was coiled at the bottom of the casing, passing through a hole at the bottom of the casing for electrical contact. The wire was secured at its position using epoxy glue. A circular shaped silver foil acted as a support to the wire, wherein the said foil was mechanically pressed onto the wire.

Approximately, equal weight ratio of silver nanoparticles (0.3 g), silver chloride crystals (0.3 g), and potassium chloride (0.3 g) were added into a glass vial. The vial was then capped tightly and shaken vigorously for about five minutes. After that, 50 µL of low impedance organic binder [15% weight of Bisphenol A propoxylate diglycidyl ether-diamine (1:1 volume ratio) in ethanol] was added dropwise to 0.2 g of the mixture. The resulting formed paste was filled into the tubular casing containing the wire and the silver foil.

The casing was manually compacted at high pressure by using a 3-mm stainless steel plunger that was positioned exactly above the paste. Finally, the silver-silver chloride-potassium chloride electrode was cured in the oven at around 100°C for about 30 minutes.

Experiment 1

A solid-state reference electrode (Solid 2) has been characterized in terms of potentiometric response with commercial chemical sensors. Commercial nitrate and potassium ion-selective electrodes (ISE) from Nico2000 were used to conduct response tests.

Figure 2 shows the responses of the nitrate ISE with standard potassium nitrate test solutions (10^{-4} to 10^{-1} M). The plots of response versus log of nitrate activity gave slope of –52 mV/decade with correlation coefficient of 0.99.

Figure 2 also shows the responses of the potassium ISE with standard potassium nitrate test solutions (10^{-4} to 10^{-1} M). The plots of response versus log of nitrate activity gave slope of 54 mV/decade with correlation coefficient of 0.98.

As can be seen in Figure 2, both slopes gave the expected sensitivity for nitrate and potassium ISE chemical sensors from Nico2000.

In conclusion, based on the results shown in this experiment, it is demonstrated that a solid-state reference electrode is suitable for potentiometric measurement.

Claims

1. A solid-state reference electrode, comprising:

silver-silver halide electrode to convert potential difference due to analyte activity to electrical signal;

halide salt to give constant activity of the halide ion and to produce reference voltage; and

low impedance organic binder to provide conductive solid medium and low impedance current path for the electrical signal.

2. The solid-state reference electrode as claimed in claim 1 wherein the said reference electrode is enclosed in a casing.

3. The solid-state reference electrode as claimed in claims 1 and 2 wherein an electrical conductor is coiled at the bottom of the casing.

4. The solid-state reference electrode as claimed in claims 1 to 3 wherein the said electrical conductor is a wire.

5. The solid-state reference electrode as claimed in claims 1 to 4 wherein the said electrical conductor is made of silver or platinum.

6. The solid-state reference electrode as claimed in claim 1 wherein the silver-silver halide electrode comprises of silver material, wherein the said silver material is at least one or combination of the following: silver nanoparticles and/or silver paste.

7. The solid-state reference electrode as claimed in claims 1 and 6 wherein the silver material is present in an amount of from around 5 to 40 % by weight.

8. The solid-state reference electrode as claimed in claim 1 wherein the silver-silver halide electrode comprises of at least one or combination of the following silver halide crystals: silver chloride, silver bromide, and/or silver iodide.

9. The solid-state reference electrode as claimed in claims 1 to 8 wherein the silver halide crystals are present in an amount of from around 5 to 40 % by weight.

10. The solid-state reference electrode as claimed in claim 1 wherein the halide salt is at least one or combination of the following halide salts: chloride salt, bromide salt, and/or iodide salt.

11. The solid-state reference electrode as claimed in claims 1 and 10 wherein the halide salt is present in an amount of from around 5 to 20 % by weight.

12. The halide salt as claimed in claims 10 and 11 wherein the positively charged counterion is at least one or combination of the following cations: lithium, sodium, potassium, imidazolium, and/or ammonium.

13. The solid-state reference electrode as claimed in claim 1 wherein the low impedance organic binder comprises one or combination of these following compounds: Bisphenol A propoxylate diglycidyl ether, methyl methacrylate-glycidyl methacrylate-tetrahydrofurfuryl acrylate copolymer, glycidyl methacrylate-tetrahydrofurfuryl acrylate copolymer, cellulose acetate, ethyl cellulose and/or cellulose.

14. The solid-state reference electrode as claimed in claims 1 and 13 wherein the low impedance organic binder is present in an amount of from around 2 to 5 % by weight.

15. The method of producing the said reference electrode wherein the silver, silver halide, halide salt and low impedance organic binder are homogenously mixed to form a thick paste and the said paste are packed into the casing, mechanically compacted at high pressure and cured at around 75 to 200°C and at high pressure for about 1 to 10 hours

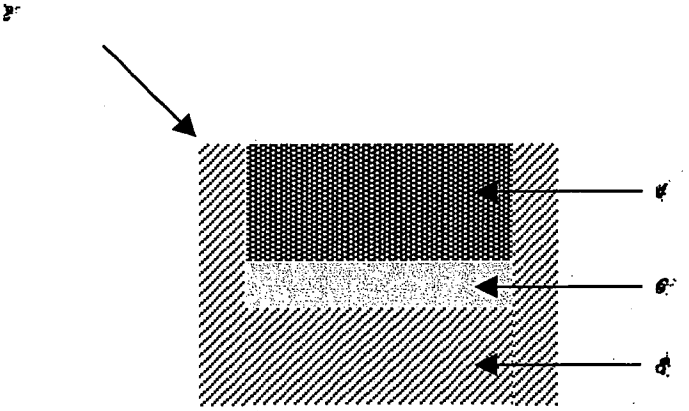


Figure 1

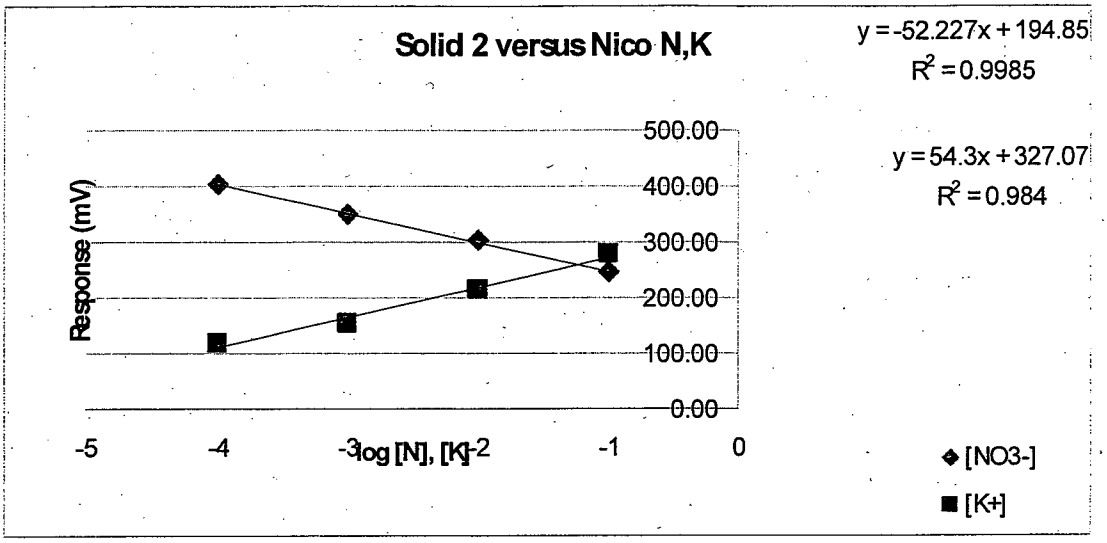
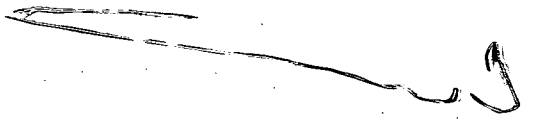


Figure 2: Response of commercial nitrate and potassium ISE sensors with fabricated all solid reference electrode (Solid 2)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2011/000095

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

G01N 27/26 (2006.01) ***G01N 27/30*** (2006.01)

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)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI and EPODOC: electrode, sensor, bio-sensor; silver, Ag; halide, fluoride, chloride, bromide, iodide; AgF, AgF2, Ag2F, AgCl, AgBr, AgI; binder, matrix, glue, adhesive; organic, polymer, copolymer, bisphenol, acrylate, cellulose, acetate; measure, sensor, G01N27/00/LOW; reference, standard, baseline; reference electrode; conductor, low resistance, low impedence; solid state; AND LIKE TERMS. Google Scholar: reference electrode; silver, Ag; silver chloride, AgCl; binder; conducting; polymer, organic; salt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0682247 A1 (SIEMENS PLESSEY CONTROLS LIMITED) 15 November 1995 Abstract, column 1 line 18 to column 3 line 21, figures 1 to 4	1-15
A	US 4857166 A (KOTANI) 15 August 1989 Abstract, column 3 line 27 to column 4 line 7, column 4 line 42 to column 9 line 34, figures 1 to 9	1-15
A	Patent Abstracts of Japan, JP 03-291557 A (FUJI PHOTO FILM CO LTD) 20 December 1991 Abstract	1-15

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 September 2011	13.09.2011
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **RICHARD BAKER** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 2583

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/MY2011/000095

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Patent Document Cited in Search Report		Patent Family Member	
EP	0682247	GB	2289540
US	4857166	JP	63138254
JP	03291557	NONE	

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX