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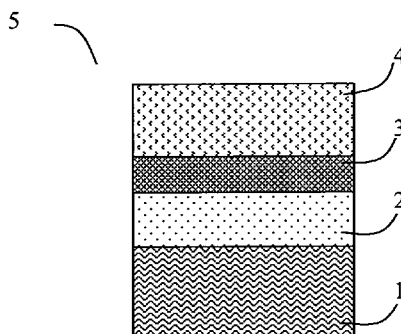


FIGURE 1

(57) Abstract: The present invention provides a solid state reference electrode comprising; polymeric substrate, silver materials, silver chloride materials; and nano-porous hybrid solgel materials doped with chloride salts and borate compounds. The present invention also provides a method for preparation of solid hydrogel comprises the steps of: (a) mixing tetraethyl orthosilicate, methyltriethoxysilane, deionized water, and hydrochloric acid; (b) stirring and mixture until a clear homogeneous mixture is achieved; (c) adding lithium chloride and trimethyl borate to the homogeneous mixture; (d) sonicating the mixture of step (c).



LEAK-FREE REFERENCE ELECTRODE WITH NANO-POROUS PROTECTIVE MEMBRANES

Technical Field

- [1] The present invention relates to a reference electrode, more particularly it relates to a solid state reference electrode with protective nano-porous membranes.

Background Art

Background Art

- [2] Quantitative analysis of ionic analyte is done based on the principle of potentiometry. Ion selective electrode (ISE) chemical sensor functions as a working electrode half cell, coupled to a reference electrode, gives voltage response close to the ideal Nernstian value. Flows of electrons in the conductive wires and ions in the liquid analyte complete the passage of current in the circuit.
- [3] Both the working and reference electrodes give equal contribution to the potentiometric response. Therefore, accuracy, stability and durability of the reference electrode is as important as the sensitivity and selectivity of the sensing membrane.
- [4] Conventional double-junction reference electrodes are suitable for laboratory use, whereas, for field deployment they are too bulky. Conventional reference electrode contains liquid internal electrolyte that gradually leaks out and likewise, ions in the external chamber and analytes contaminate the inner reference electrolyte. Regular maintenance that includes thorough cleaning, drying and replacement of electrolyte is necessary to ensure reliable measurement using double-junction reference electrode - this is not possible for *in situ* measurements in soils and fluids.

Disclosure of Invention

Technical Problem

[5]

Technical Solution

[6]

Summary

- [7] The present invention relates to preparation of reference electrode for potentiometric electrochemical measurement. More specifically, the invention relates to preparation of leak-free miniaturized reference electrode that does not require regular maintenance and suitable for long term field deployment.
- [8] The present invention provides miniaturized leak-free reference electrode that doesn't require any maintenance and suitable for long term field deployment. We disclose a

reliable reference electrode that contains constant concentration of reference electrolyte and thus gives stable response readings. The invention can be manufactured in volume production as stand-alone reference half cell components that can be integrated in potentiometric system such as chemical sensor equipped with a display or RF transmitter.

- [9] The present invention provides a solid state reference electrode comprising: polymeric substrate, silver materials, silver chloride materials; and nano porous hybrid solgel materials doped with chloride salts and borate compounds.
- [10] The present invention also provides a method for preparation of solid hydrogel comprises the steps of: (a) mixing tetraethyl orthosilicate, methyltriethoxysilane, deionized water, and hydrochloric acid; (b) stirring the mixture until a clear homogenous mixture is achieved; (c) adding lithium chloride and trimethyl borate to the homogenous mixture; (d) sonicating the mixture of step (c);
- [11] The present invention provides miniaturized leak-free reference electrode by preventing loss of reference electrolyte using protective membranes as described in Figures 1 and 2.
- [12] The present invention also provide a reference electrode that can be manufactured in a few fabrication steps, and it can be employed in potentiometric chemical sensors with good stability and durability.

Description of Drawings

- [13] **Brief description of the drawings**
- [14] **FIGURE.1** : illustrates an embodiment of layer composition of protective membranes.
- [15] **FIGURE.2** : illustrates response of Nico2000 nitrate sensor versus a reference electrode based on nano-porous membrane.
- [16] **FIGURE.3** : illustrates signal stability of a reference electrode based on nano-porous membrane
- [17] **FIGURE.4** : illustrates result of chloride leakage test by precipitation with silver nitrate

- [18]
- [19] **Detailed description of the preferred embodiment of the present invention**

Examples

Example 1

Solid-State Reference Electrode

- [22]
- [23] **FIGURE. 1** illustrates one preferred embodiment of solid-state reference electrode 5 of the present invention. Substrate 1 is strong polymeric material that gives physical strength of the reference electrode and is compatible with the screen-printed silver paste. Polyester, polycarbonate, printed circuit board having thickness of 0.3 to 1mm thickness are suitable substrate materials. Layer 2 screen-printed silver materials from

appropriate paste mixture, printed through a mask to give circular shape having 3 to 8 mm diameter. The printed silver paste is cured at the temperature of 80 to 150° C to give final dry thickness of 50 to 500micrometer. Silver chloride layer 3 is grown from the silver material by chlorination process using ferric chloride solution having concentration of 0.1M to 1M for 30 to 120 seconds in the absence of light. Nano-porous membrane 4 is hybrid solgel material doped with chloride salts and borate compounds. The hybrid solgel composition is deposited onto the circular silver-silver chloride electrode, followed by curing and sintering process in the oven at the temperature of 50 to 130° C. A few crystals of potassium chloride (KCl) can be added on top of the silver-silver chloride electrode before dispensing of the hybrid solgel cocktail. This can function as an internal reference of constant chloride concentration.

[24] **Composition of Nanoporous Glassy Membrane**

[25] Cocktails for nano-porous membranes were prepared from the compositions provided in Table 1.

[Table 1]

[Table]

Tetraethyl ortho silicate	Methyl-triethox ysilane	Phenyl-triethox ysilane	Trimethylborate Đ	Lithium Chloride
20 - 60 %	20 - 60 %	20 - 60 %	0.5 – 5%	0.5 – 5%

[26] Table 1: composition nano-porous membrane

[27]

[28] **Example 2**

[29] **Preparation of Hybrid Solgel Nano-porous Membrane**

[30] Tetraethyl orthosilicate (TEOS, 450 uL), 450 uL of methyltriethoxysilane (MTES), 280 uL of deionized water (DIW) and 20 uL of 0.1M hydrochloric acid are mixed in a glass vial or round-bottom flask.

[31] The mixture was stirred for 4 hours until a clear solution was achieved. Then, 200 uL of the homogenous mixture was mixed with lithium chloride (LiCl) to get 0.5% LiCl by weight and trimethyl borate (TMB) to get 0.5 % TMB by weight and the mixture sonicated for 60 minutes.

[32] Screen printed silver-silver chloride electrode having circular shaped with 4mm diameter, printed on polyester or FR4 substrate with 0.5mm thickness was dipped into the hybrid solgel cocktail containing 0.5% LiCl and 0.5% TMB, both by weight. The electrode was dried in open air for 10 minutes and the drying process was continued under nitrogen blanket for another 10 minutes

[33] After the ambient temperature drying process, the electrode underwent low-temperature sintering cycles at three different temperatures. First the electrode was

heated in the oven at 50°C for 10 minutes and later at 70°C for 10 minutes and finally at 100°C for 10 minutes.

[34] **Response with Chemical Sensor**

[35] As illustrated in FIGURE.2 The response of commercial Nico 2000 nitrate ion-selective electrode versus three reference electrode based on nano-porous glassy membrane has been examined. FIGURE.8 shows the three reference electrodes give comparable response signals and slope with a common working electrode. Three solid-state reference electrodes with nano-porous hybrid solgel membrane on FR4 substrate, prepared using the above procedure, have been characterized for its responses with ion selective electrode nitrate sensor. The reference electrode and Elite Nico2000 nitrate sensor were both immerse in 10^{-4} M to 10^{-1} M of potassium nitrate solutions. The response readings from these measurement were taken and the data plotted as shown in the following figure. The results show that the reference electrode with doped hybrid solgel membrane can function as reference for potentiometric measurement. Moreover, the three reference electrodes give similar response signal with the nitrate sensor.

[36] **Signal Stability and Drift**

[37] FIGURE.3 The solid-state reference electrode with nano-porous hybrid solgel membrane on FR4 substrate, prepared using the above procedure, has also been subjected to signal stability and drift test. A commercial calomel reference electrode and a freshly fabricated reference electrode were immersed in 10^{-3} M solution of potassium chloride. Both electrodes were connected to an ion meter the the response signal response signals recorded every minute for 30 minutes. The results were plotted as shown in the following graph. The data show that the reference electrode based on doped hybrid solgel membrane gives very stable signal and suitable to be used for potentiometric measurement.

[38] **Leakage Test**

[39] Loss of chloride reference electrolyte from the reference electrode was characterized by precipitation of silver chloride. The freshly fabricated reference electrode was dipped into a glass vial containing deionized water and allowed to stand at room temperature or warmed at 50 °C for 20 hours. Silver nitrate solution (1M) was titrated into the solution until there was no noticeable change in color. Silver chloride precipitate first appears as white cloud.

[40] FIGURE. 4 illustrate comparison of silver chloride leakage between conventional and hybrid solgel glassy membrane. The intensity of the white color suggests the amount of silver chloride formed. Upon standing for a few hours, the white cloud disappeared and dark silver chloride crystals formed at the bottom of the vial. Minimal chloride loss gives almost clear solution upon titration with silver nitrate.

[41] Although the preferred embodiments of the present invention have been described

herein, the above descriptions are merely illustrative. Further modification of the invention herein disclosed will occur to those skilled in the respective arts and all such modifications are deemed to be within the scope of the invention as defined by the appended claims.

Best Mode

[42]

Mode for Invention

[43]

Industrial Applicability

[44]

Sequence List Text

[45]

Claims

[Claim 1]

1. A solid state reference electrode **5** comprising;
polymeric substrate (**1**),
silver materials (**2**),
silver chloride materials (**3**); and
nano-porous hybrid solgel materials (**4**) doped with chloride salts and borate compounds.
2. A solid state reference electrode **5** according to claim 1 characterised in that the silver materials (**2**) is screen printed, cured at 80 to 150° C to give final dry thickness of 50 to 500micrometer.
3. A solid state reference electrode **5** according to claim 1 characterised in that the silver chloride materials (**3**) is grown from the silver material by chlorination process using ferric chloride solution having concentration of 0.1M to 1M for 30 to 120 seconds in the absence of light.
4. A solid state reference electrode **5** according to claim 1 characterised in that the nano-porous hybrid solgel composition (**4**) wherein the solgel cocktail contains, tetraethylorthosilicate, methyltriethoxysilicon, phenyltriethoxysilicon, chloride salt and borate compound.
5. A solid state reference electrode **5** according to claim 4 characterised in that the solgel cocktail contains 20 to 60% of tetraethylorthosilicate, 20 to 60% of methyltriethoxysilicon, 20 to 60% of phenyltriethoxysilicon, 1 to 5% of chloride salt and 1 to 5% of borate compound.
6. A solid state reference electrode **5** according to claim 5 characterised in that the chloride salt is selected from the list of the chloride salt of lithium, sodium or potassium.
7. A solid state reference electrode **5** according to claim 5 characterised in that the borate compound is trimethyl borate or triethylborate.
8. A method for preparation of solid hydrogel comprises the steps of:
 - a) mixing tetraethyl orthosilicate, methyltriethoxysilane, deionized water, and hydrochloric acid;
 - b) stirring the mixture until a clear homogeneous mixture is achieved;
 - c) adding lithium chloride and trimethyl borate to the homogeneous mixture;
 - d) sonicating the mixture of step (c);
9. A composition of hybrid solgel for use in preparation of a solid-state

reference electrode comprises of tetraethyl orthosilicate, methyltriethoxysilane, phenyltriethoxysilane, lithium chloride and trimethyl borate.

10. A method for preparing a solid state reference electrode comprises the steps of:

- a) dipping a silver-silver chloride electrode into cocktail of hybrid solgel;
- b) drying the electrode under nitrogen condition; and
- c) sintering the electrode at low temperatures.

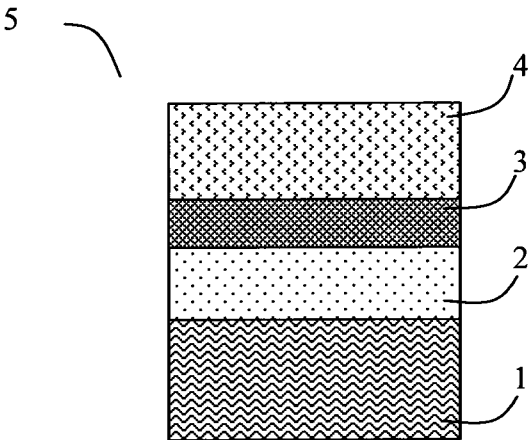


FIGURE 1

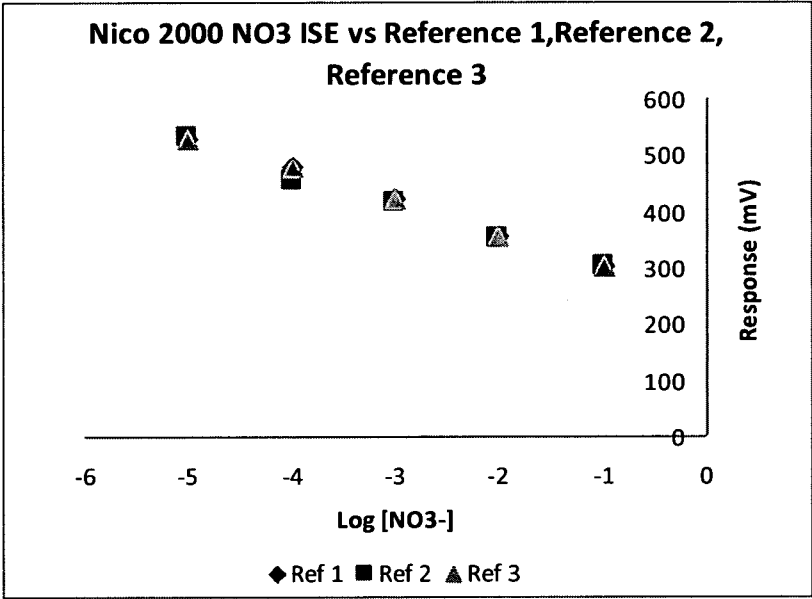


FIGURE 2

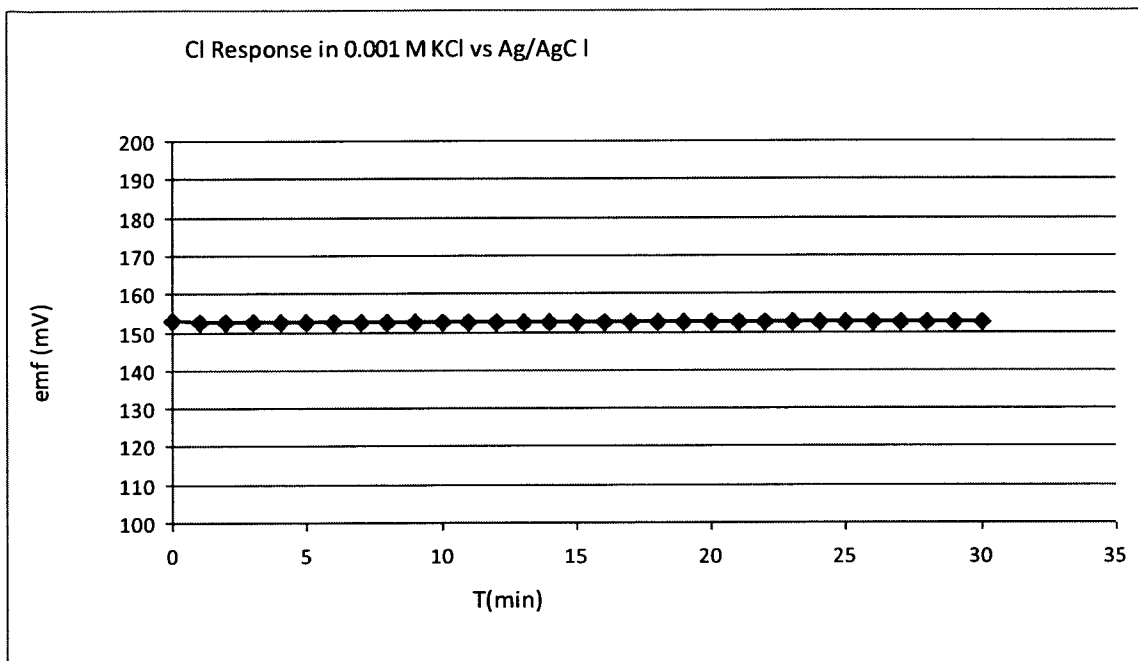


FIGURE 3



FIGURE 4