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(54) **Title:** A DOUBLE JUNCTION REFERENCE ELECTRODE

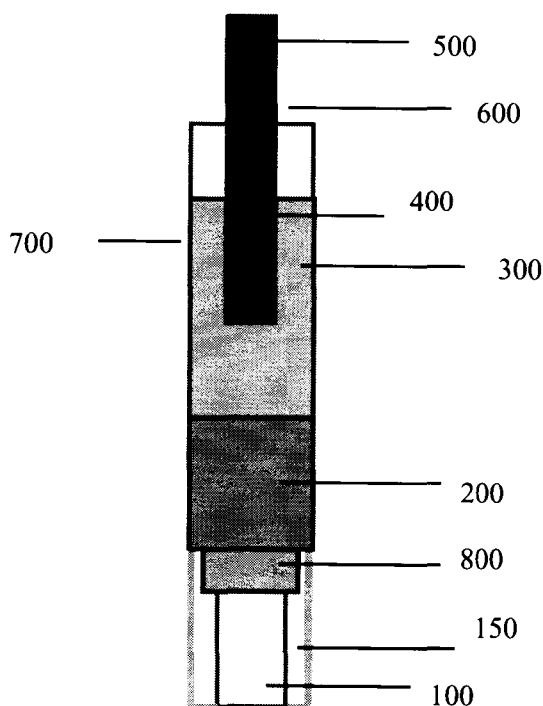


Figure 1

(57) **Abstract:** The present invention relates to a double junction reference electrode comprising: a porous plug (100); a leak protection cap (150); an external electrolyte (200); an internal reference (300); a silver-silver chloride electrode (400); a silver wire (500); a cap (600); and a casing (700); characterised in that the external electrolyte (200) further comprising halide-free electrolyte in gelled medium including a leak free protection seal (800) to provide internal sealing for the space between the porous plug (100) and the electrolytes and to cover the entire porous plug (100) inside with porous membrane. The present invention provides better performance of the reference electrode since leakage of the electrolyte is tackled with above mechanism.



GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Description

Title of Invention: A DOUBLE JUNCTION REFERENCE ELECTRODE

[1] **FIELD OF INVENTION**

[2] The present invention relates to a double junction reference electrode of a chemical sensor.

[3] **BACKGROUND OF THE INVENTION**

[4] One problem with reference electrodes is that, in order to ensure a stable voltage, it is necessary to maintain a steady flow of electrolyte through the porous frit. Thus there is a gradual contamination of the test solution with electrolyte ions. This can cause problems when trying to measure low levels of K, Cl, or Ag, or when using other ISEs with which these elements may cause interference problems.

[5] In order to overcome this difficulty the double junction reference electrode was developed. In this case the silver-silver chloride cell forms the inner element and this is inserted into an outer tube containing a different electrolyte which is then in contact with the outer test solution through a second porous frit. The outer filling solution is said to form a 'salt bridge' between the inner reference system and the test solution and is chosen so that it does not contaminate the test solution with any ions which would affect the analysis.

[6] However, the available reference electrode of the chemical sensors suffer from chloride ion interference due to the leakage of reference electrode electrolyte. For single-junction reference electrode, leakage of reference electrolyte would contaminate the analyte. In silver-silver chloride reference electrode, the reference electrolyte is chloride (a halide). Chloride or other halide ions are main interfering ion in anion sensor such as nitrate and phosphate sensors and thus halide contamination from reference electrode is not desirable.

[7] Therefore, there is a need for an invention which tackles halide leakage and interference on the reference electrode.

[8] **SUMMARY OF THE INVENTION**

[9] According to an aspect of the present invention, the present invention provides a double junction reference electrode comprising: a porous plug (100) to allow external electrolyte to pass through; a leak protection cap (150) to encapsulate the porous plug (100) and to expose only the tip of the porous plug (100); an external electrolyte (200) to provide solid medium in order to support the internal reference and to provide ions for signal conduction; an internal reference (300) to provide constant concentration of chloride; a silver-silver chloride electrode (400) to provide reversible reduction-

oxidation characteristic for electrochemical transduction; a silver wire (500) to conduct electrical signal and to provide substrate for silver-silver chloride electrode; a cap (600) to protect internal reference and to provide inlet for refilling; and a casing (700) to provide mechanical support for the porous plug (100), electrolytes and entire assembly; characterised in that the external electrolyte (200) further comprising halide-free electrolyte in gelled medium including a leak free protection seal (800) to provide internal sealing for the space between the porous plug (100) and the electrolytes and to cover the entire porous plug (100) inside with porous membrane.

- [10] The above provision is advantageous as the use of the leak free protection seal (800) and the gelled medium of the external electrolyte (200) minimize the possibility of the electrolyte to leak thus jeopardizing the performance of the reference electrode as a whole.
- [11] Leaking of chloride internal reference in reference electrode causes interference in the measurement and sensing of anionic analytes such as phosphate, nitrate and sulfate.
- [12] The present invention provides a double junction reference electrode with negligible presence of chloride ion, which is suitable for portable and field application. The present invention provides the porous plug (100) is completely sealed to prevent leakage, externally the entire plug (100) is encapsulated only to expose the tip. The interior part of the plug (100) is fully covered with membrane, and the space between plug and body is sealed as well.
- [13] The present invention also provides the internal reference is separated from the analyte by the halide free solid external electrolyte (200). The state of the external electrolyte (200) which is in solid medium supports the internal reference as well.
- [14] **BRIEF DESCRIPTION OF THE DRAWINGS**
- [15] **Figure 1** illustrates an embodiment of a double junction reference electrode of the present invention.
- [16] **Figure 2** illustrates a flowchart of a method of preparing a double junction reference electrode of the present invention.

[17] **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

- [18] Generally, the present invention relates to a double junction reference electrode comprising: a porous plug (100) to allow external electrolyte to pass through; a leak protection cap (150) to encapsulate the porous plug (100) and to expose only the tip of the porous plug (100); an external electrolyte (200) to provide solid medium in order to support the internal reference and to provide ions for signal conduction; an internal reference (300) to provide constant concentration of chloride; a silver-silver chloride electrode (400) to provide reversible reduction-oxidation characteristic for electrochemical transduction; a silver wire (500) to conduct electrical signal and to provide substrate for silver-silver chloride electrode; a cap (600) to protect internal reference

and to provide inlet for refilling; and a casing (700) to provide mechanical support for the porous plug (100), electrolytes and entire assembly; characterised in that the external electrolyte (200) further comprising halide-free electrolyte in gelled medium including a leak free protection seal (800) to provide internal sealing for the space between the porous plug (100) and the electrolytes and to cover the entire porous plug (100) inside with porous membrane. This is illustrated in **Figure 1**.

- [19] The porous plug (100) comprises of at least one of the following materials: ceramic, alumina, zirconia, glass, cellulose, sol gel. The cap (600) comprises at least one of the following materials: epoxy, polyvinyl chloride, polycarbonate, polyester, glass, ceramic, zirconia, teflon, polyethylene. The material of the external electrolyte (200) gel is from hydroxyethyl methacrylate, or acrylamide, or glycidyl methacrylate, or methyl methacrylate, or butyl acrylate, or tetrahydrofurfuryl acrylate. The material of the leak free protection seal (800) is from acrylic, or cellulose acetate, or cellulose, or cellulose nitrate, or polyurethane, or polyvinyl chloride, or glass, or ceramic, or zirconia. The ion of the external electrolyte is from ion of acetate; or trifluoroborate; or perchlorate; or nitrate; or sulfate; or phosphate; or phosphorate; or borate; or tri-fluoroacetate; or styrene sulfate; or toluene sulfate, nafion, polyanethole sulfate, hexafluorophosphate.
- [20] As illustrated in **Figure 2**, in general, the method of preparing the solid state double junction comprising: sealing an external porous plug to expose only the tip (10); sealing an internal porous plug with porous material (20); preparing an external electrolyte gel (30); filling the internal reference electrolyte (40); capping a refill inlet with silver-silver electrode assembly (50); and testing electrolyte leak rate and sensor response signals (60).
- [21] The encapsulation and sealing of the porous plug of the step (10) is started with freshly cut and cleared zirconia rod (2 mm) is secured at the narrow-end tip. Cellulose acetate solution (50 μ L, 5 wt%) is cast on the porous plug (100). Epoxy heat curable adhesive is applied onto the external porous plug, exposing only the tip. The plug assembly is treated with heat in the oven at 90°C for one hour.
- [22] For more detail of the preparation of the external electrolyte (200), the procedure is started with hydroxyethyl methacrylate (5 mL, 0.1 M) lithium acetate and ammonium persulphate (trace) are homogeneously mixed and filled into the plugged assembly, the assembly is clamped, immersed in water and heated at boiling temperature for one hour.
- [23] Although the invention has been described with reference to particular embodiment, it is to be understood that the embodiment is merely illustrative of the principles and applications of the present invention. It is therefore to be understood that numerous modifications may be made to the illustrative embodiment that other arrangements

may be devised without departing from the scope of the present invention as defined by the appended claims.

Claims

- [Claim 1] A double junction reference electrode comprising:
a porous plug (100) to allow external electrolyte to pass through;
a leak protection cap (150) to encapsulate the porous plug (100) and to expose only the tip of the porous plug (100);
an external electrolyte (200) to provide solid medium in order to support the internal reference and to provide ions for signal conduction;
an internal reference (300) to provide constant concentration of chloride;
a silver-silver chloride electrode (400) to provide reversible reduction-oxidation characteristic for electrochemical transduction;
a silver wire (500) to conduct electrical signal and to provide substrate for silver-silver chloride electrode;
a cap (600) to protect internal reference and to provide inlet for refilling; and
a casing (700) to provide mechanical support for the porous plug (100), electrolytes and entire assembly;
characterised in that
the external electrolyte (200) further comprising halide-free electrolyte in gelled medium including a leak free protection seal (800) to provide internal sealing for the space between the porous plug (100) and the electrolytes and to cover the entire porous plug (100) inside with porous membrane.
- [Claim 2] A double junction reference electrode as claimed in Claim 1, wherein the material of the external electrolyte (200) gel is from hydroxyethyl methacrylate, or acrylamide, or glycidyl methacrylate, or methyl methacrylate, or butyl acrylate, or tetrahydrofurfuryl acrylate.
- [Claim 3] A double junction reference electrode as claimed in Claim 1, wherein the material of the leak free protection seal (800) is from acrylic, or cellulose acetate, or cellulose, or cellulose nitrate, or polyurethane, or polyvinyl chloride, or glass, or ceramic, or zirconia.
- [Claim 4] A double junction reference electrode as claimed in Claim 1, wherein the ion of the external electrolyte (200) is from ion of acetate; or trifluoroborate; or perchlorate; or nitrate; or sulfate; or phosphate; or phosphorate; or borate; or trifluoroacetate; or styrene sulfate; or toluene sulfate, nafion, polyanethole sulfate, hexafluorophosphate.
- [Claim 5] A method of preparing the solid state double junction comprising:

- i. Sealing an external porous plug to expose only the tip (10);
- ii. Sealing an internal porous plug with porous material (20);
- iii. Preparing an external electrolyte gel (30);
- iv. Filling the internal reference electrolyte (40);
- v. Capping a refill inlet with silver-silver electrode assembly (50); and
- vi. Testing electrolyte leak rate and sensor response signals (60).

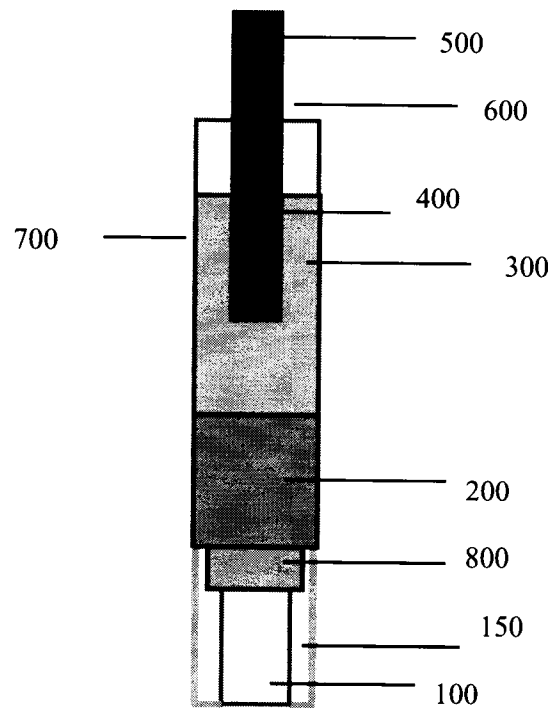


Figure 1

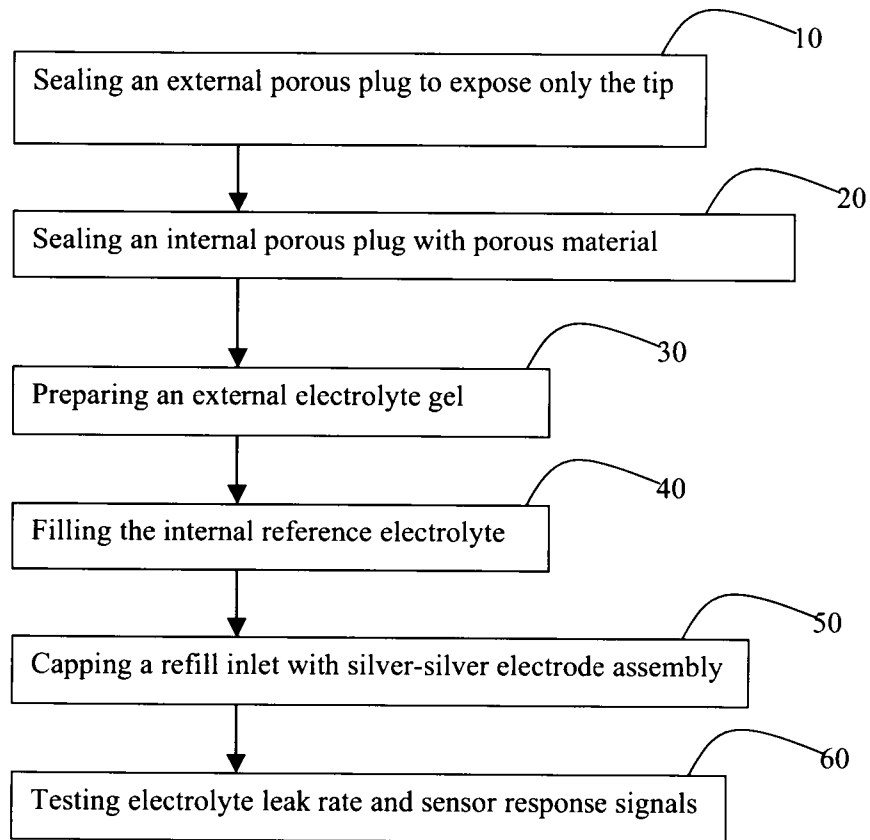


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/MY2014/000096

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N27/30
ADD.

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

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)

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 282 081 A (ARRANCE SR FRANK C) 4 August 1981 (1981-08-04) the whole document	1-5
A	----- WO 2011/155815 A1 (MIMOS BERHAD [MY]; AHMAD DR RAIS AHMAD [MY]; ALVA DR SAGIR [MY]; TUHAI) 15 December 2011 (2011-12-15) the whole document	1-5
A	----- WO 93/04360 A1 (KODAK PATHE [FR]; KODAK LTD [GB]; EASTMAN KODAK CO [US]) 4 March 1993 (1993-03-04) the whole document	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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