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(71) Applicant *(for all designated States except US)*: **MIMOS BERHAD** [MY/MY]; Technology Park of Malaysia, 57000 Kuala Lumpur (MY).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **AHMAD, Mohd, Rais** [MY/MY]; Mimos Berhad, Technology Park Malaysia, Bukit Jalil, 57000 Kuala Lumpur (MY). **ALVA, Sagir** [ID/MY]; Mimos Berhad, Technology Park Malaysia, Bukit Jalil, 57000 Kuala Lumpur (MY).

(74) Agent: **NAWAWI, Norunnuha**; Ipsynthesis SDN BHD, 32-1-1B, Jalan Medan PB2B, Seksyen 9, Pusat Bandar Baru Bangi, 43650 Selangor (MY).

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(54) **Title**: A CHARGE-BALANCED PLANAR REFERENCE ELECTRODE

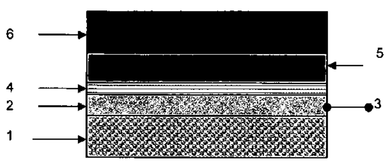

Figure 1

(57) **Abstract**: This invention relates to reference electrode used as half cell in potentiometric measurement. More specifically, the invention is directed to preparation of planar reference electrode containing highly lipophilic cation and anion components that function to balance the total of positive and negative charges approaching the chloride internal electrolyte.

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A CHARGE-BALANCED PLANAR REFERENCE ELECTRODE

FIELD OF THE INVENTION

This invention relates to reference electrode used as half cell in potentiometric measurement. More specifically, the invention is directed to preparation of planar reference electrode containing highly lipophilic cation and anion components that function to balance the total of positive and negative charges approaching the chloride internal electrolyte.

BACKGROUND OF THE INVENTION

Detection of various chemical species such as cation, anions, electrophilic or neucleophilic particles normally uses electrochemical sensors specifically designed for the determination of a particular chemical species' concentration, more accurately described as its activity, in a solution. The determination is based on the fact that within certain limits, the potential of the electrode is directly proportional to the logarithm of the chemical species' activity. These electrochemical sensors generally have sensing membranes specifically formulated for measuring the chemical species of interest. One of the important properties of an electrochemical sensor is its selectivity. Meaning that, the results that are obtained are highly independent of other chemical species/ions which are present in the sample being tested.

Selective membrane sensors originated in the basic pH glass membrane electrode. The advent of crystal and liquid membrane sensors led to the development of ion-selective electrodes. Combining these sensors with microporous synthetic membranes resulted in electrochemical sensors for measuring carbon and sulfur dioxide, ammonia, hydrogen sulfide, and other dissolved gases in blood urine and body fluid samples. Coupling biological reagents to gas sensors and ion-selective electrodes resulted in biosensor systems involving enzymes, bacteria, tissue cells, and immuno-agents.

Other types of sensors have also been developed which include affinity, enzyme-linked immunoadsorbent, immune-complex, antigen, and antibody sensors. The ion-selective electrode (ISE) is the key element of many biosensors.

ISEs have many applications in the fields of medicine, engineering, industrial processing control, education, and research. They are especially useful in clinical and environmental chemistry where large numbers of samples are processed.

Basically, the sensing membrane is made of glass or various polymers such as polyvinyl chloride (PVC), silicone and the like. Sensors using glass membranes such as sensors for pH and sodium are relatively resistant to leaching under normal test conditions. Even when used in media such as human serum containing lipophilic agents, a glass-membrane type sensor can usually be cleaned and reconditioned thus extending the sensor's useful life. A polymeric-membrane type ISE, on the other hand, is more sensitive to the conditions that cause failure, thus having a much shorter useful life as compared to glass-membrane type sensors. One of these conditions is the presence of interfering ions or substances.

Various attempts have been made in the past to couple multiple sensors together and to prolong sensor life.

Therefore, what is needed is an ISE that has a longer uselife and better performance than ISEs currently available. The use life of an ISE is defined as the length of time an ISE continues to function properly and reliably for its intended use. Hence, we propose planar reference electrode that can be integrated on the same platform with chemical multi-sensors, whereby the stability of reference electrode is achieved through charge balancing mechanism.

SUMMARY OF THE INVENTION

This invention relates to reference electrode used as half cell in potentiometric measurement. More specifically, the invention is directed to preparation of planar reference electrode containing highly lipophilic cation and anion components that function to balance the total of positive and negative charges approaching the chloride internal electrolyte.

It is an object of the present invention to provide a planar reference electrode that doesn't require the use of liquid electrolytes or any maintenance.

It is another object of the present invention to provide a planar reference electrode that is miniaturized and integrated on the same planar platform with the multi-sensors.

It is yet another object of the present invention to provide a planar reference electrode that is leak-free and doesn't suffer from loss of ionic electrolytes.

It is a further object of the present invention to provide a planar reference electrode that is durable and suitable for field deployment.

The method, setup, materials, polymer and molecules described in the invention are directed towards preparation of planar reference electrode based on charge-balanced mechanism.

The reference electrode is to be integrated with chemical multi-sensors and to be deployed preferably for precision agriculture and environmental monitoring.

All of the advantages of the present invention will be clear upon review of the detailed description, drawings and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 illustrates the preferred embodiment of a charge-balanced planar reference electrode.

Fig.2 illustrates an immobilized ammonium borate salts for charge-balanced reference electrode.

Fig.3 illustrates chloride response from charge-balanced planar reference electrode versus conventional double-junction reference electrode.

Fig.4 illustrates K+ response of a commercial potassium sensor versus charge-balanced planar reference electrode.

DETAILED DESCRPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment of the proposed charge-balanced reference electrode **10** is described in Fig. 1. Substrate **11** can be polyester, polycarbonate, printed circuit board or silicon wafer. The second layer is silver-silver chloride electrode **12**, whereby the silver is electroplated or screen printed, and silver chloride is formed by chlorination of silver using ferric chloride. Electrical connection **13** to readout circuit is done using silver or copper wire. Internal layer **14** of the membrane is achieved by photo-polymerization of hydroyethyl methacrylate (HEMA) monomer and conditioning of the photocured membrane with 0.1M potassium chloride. The charge-balanced membrane **15** is formed by photocuring n-butylacrylate (nBA) containing 2% weight of immobilized ammonium borate. The top-most layer **16** is micro-porous organic polymer such as cellulose acetate for physical protection.

EXAMPLE 1

Preparation of Ag/AgCl electrode

Silver-silver chloride electrode **12** is built either using screen printed silver paste or metallic silver disc. Screen printed silver is deposited by printing silver paste through fine mesh and curing in oven at 120°C. Reproducible thickness (30 ± 2 micrometer) of dry shiny silver can be manufactured using this method. Silver discs of 3 millimeter diameter and 0.8 millimeter thickness were cut out from 99.99% silver foil, commercially available, and polished with fine sand paper before chlorination.

Chlorination of silver paste or metallic disc was achieved by ferric chloride solution ($FeCl_3$ 1 M). The solution was dropped onto the surface of printed or metallic silver and left for 2 minutes under nitrogen gas (N_2) flow for to form the Ag/AgCl electrode shown in Fig. 1 and rinsed with deionozed water, wiped and dried at ambient temperature.

Preparation of internal reference layer

After the silver-silver choride electrode Ag/AgCl **13** layer growths, HEMA monomer was deposited onto the Ag/AgCl surface and photocured with ultraviolet light for 180 seconds under nitrogen gas (N_2) flow. Poly (HEMA) membrane formed was hydrated with concentrated salts solution of potassium chloride for 1 hour. This membrane functions as internal layer **14** as showed in Figure 1.

Preparation of charge-balanced membrane

The charge-balanced membrane **15** is built by depositing cocktail of n-butyl acrylate containing 2% by weight immobilized ammonium borate and 1% of commercial photo-initiator. Approximately 1 - 5 microliter of the cocktail yields the desired thickness of 50 to 100 micrometer of photocured membrane thickness.

Preparation of insulation layer

The top-most layer **16** serves as protection or insulation layer and it is microporous in nature. Organic polymer containing polar substituent such as cellulose acetate or cellulose nitrate can be used. Cocktail (0.5 to 2 microliter) of 10% cellulose acetate in tetrahydrofuran or dioxane is deposited on photocured charge-balanced membrane. The charge-balanced membrane **16** contains 2% by weight of immobilized ammonium borate salt illustrated in Fig. 2. The ammonium ion creates lipophilic sites in the membrane to neutralize incoming negative ions. Likewise borate ion creates negatively charged sites to neutralize incoming positively charged ions.

Chloride (Cl^-) response from charge-balanced planar reference electrode versus conventional double-junction reference electrode

The response of chloride from different concentration of potassium chloride solutions produced by charge-balanced planar reference electrode versus commercially available double-junction reference electrode is illustrated in Fig. 3. The result shows that the disclosed charge-balanced planar reference electrode shows negligible potential different across a wide range of analyte activities.

Potassium ion (K^+) response of a commercial potassium sensor versus charge-balanced planar reference electrode

The response of potassium ion using commercial solid state potassium sensor versus charge-balanced planar reference electrode is described in Fig. 4. The result shows that the disclosed charge-balanced reference electrode can be used in potentiometric measurement to produce the expected response and sensitivity of the commercial reference electrode.

Additionally, the proposed planar reference electrode **10** does not require any liquid electrolyte or maintenance. It is suitable for field deployment of integrated multi-sensors for analysis of soil macronutrients and monitoring of ionic environmental contaminants. Stable reference electrode based on silver-silver chloride electrode can be achieved if the concentration of the chloride internal electrode can be made constant.

Highly lipophilic borate and ammonium are doped in hydrophobic membrane such as acrylate. Equal amount of cations and anions can be transported from the analyte to the silver-silver chloride surface with appropriate ratio of highly lipophilic borate and ammonium. The lipophilic ammonium cation is immobilized to the polymer backbone in order to avoid leaching and loss of ions.

Alternatively, inclination towards positive or negative slope can be compensated by addition of appropriate component to further balance the charge and flatten the slope. The fabricated charge-balanced planar reference electrode was characterized for stability over a wide concentration range, and coupled with commercial solid state chemical sensor for potentiometric response analysis.

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.

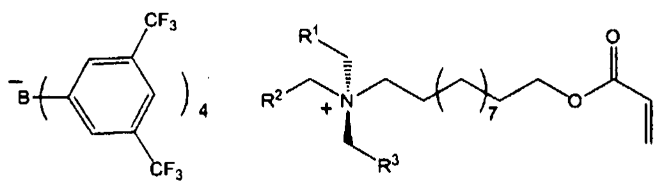
CLAIMS

1. A planar reference electrode **10** comprising:
   a substrate **11** as a first layer;
   an electrode **12** as a second layer;
   an electrode connecting part **13** to connect the electrode to a read out circuit; an internal reference layer **14**;
   a charge balanced membrane **15**;
   an insulating membrane **16**; characterised in that the charge balanced membrane **15** is immobilized with charge balancing species.

2. The planar reference electrode **10** according to claim 1 characterised in that the charge balancing species include cations and anions having similar size and migration rate.

3. The planar reference electrode **10** according to claim 1 characterised in that the charge balancing species is lipophilic ammonium and borate ions.

4. The planar reference electrode **10** according to claim 4 characterised in that the ammonium borate salts of formula 1



is used to create lipophilic ionic sites, and to achieve balanced charge at silver-silver chloride reference surface.

5. The planar reference electrode **10** according to claim 3 or claim 4 characterised in that the ammonium ion side chain R_1, R_2 and R_3 is an alkyl group.

6. The planar reference electrode **10** according to claim 5 characterised in that the alkyl group for R_1 and R_2 is preferably heptyl, $(CH_2)_6CH_3$ or undecyl, $(CH_2)_{10}CH_3$.

7. The planar reference electrode **10** according to claim 6 characterised in that the side chain R_3 is haloalkyl.

8. The planar reference electrode **10** according to claim 7 characterised in that the haloalkyl is preferably fluoroalkyl

9. The planar reference electrode 10 according to claim 8 characterised in that the fluoroalkyl is preferably $CH_2(CF_2)_7CF_3$.

10. The planar reference electrode **10** according to claim according to claim 1 characterised in that the charge balancing membrane **15** is built by depositing cocktail of n-butyl acrylate containing preferably 2% by weight immobilized ammonium borate and 1% of commercial photo-initiator.

11. The planar reference electrode **10** according to claim 1 characterised in that the charge balancing membrane **15** thickness is preferably within the range of 50 to 100 micrometer.

12. The planar reference electrode **10** according to claim 1 characterised in that the insulating membrane is microporous.

13. The planar reference electrode **10** according to claim 1 characterised in that the insulating membrane **16** is preferably made from organic polymer containing polar substituent.

14. The planar reference electrode **10** according to claim 13 characterised in that the organic polymer is selected from cellulose acetate or cellulose nitrate.

15. The planar reference electrode **10** according to claim 1 characterised in that the substrate **11** is selected from the list of polyester, polycarbonate, printed circuit board or silicon wafer.

16. The planar reference electrode **10** according to claim 1 characterised in that the electrode connecting part **13** is made of copper or silver.

17. The planar reference electrode **10** according to claim 1 characterised in that the internal layer **14** of the membrane is preferably prepared by photo-polymerization of hydroyethyl methacrylate (HEMA) monomer and conditioning of the photocured membrane with 0.1M potassium chloride.

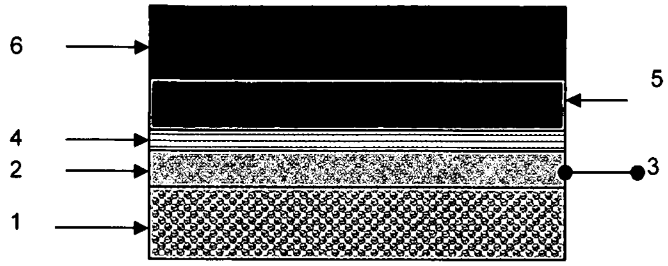
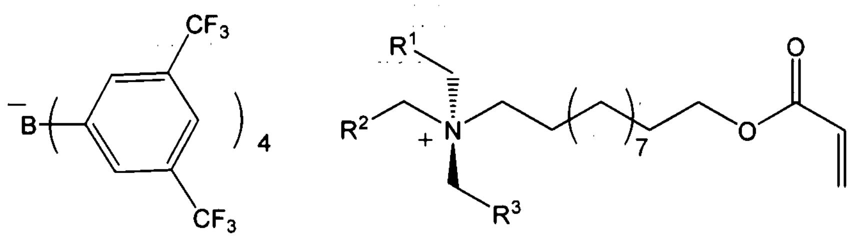


Figure 1



1: $R^1=R^2=R^3= (CH_2)_{10}CH_3$

2: $R^1=R^2= (CH_2)_{10}CH_3$; $R^3= CH_2(CF_2)_7CF_3$

3: $R^1=R^2=R^3= (CH_2)_6CH_3$

Figure 2

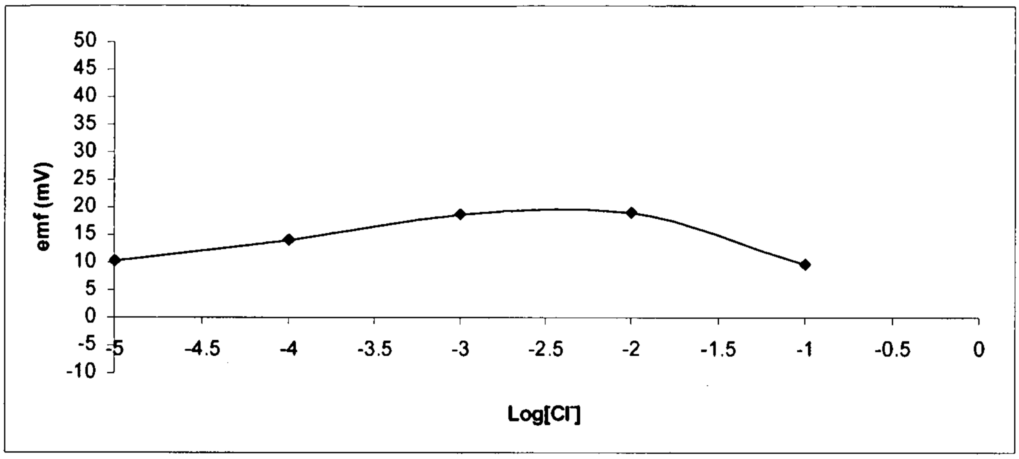


Figure 3

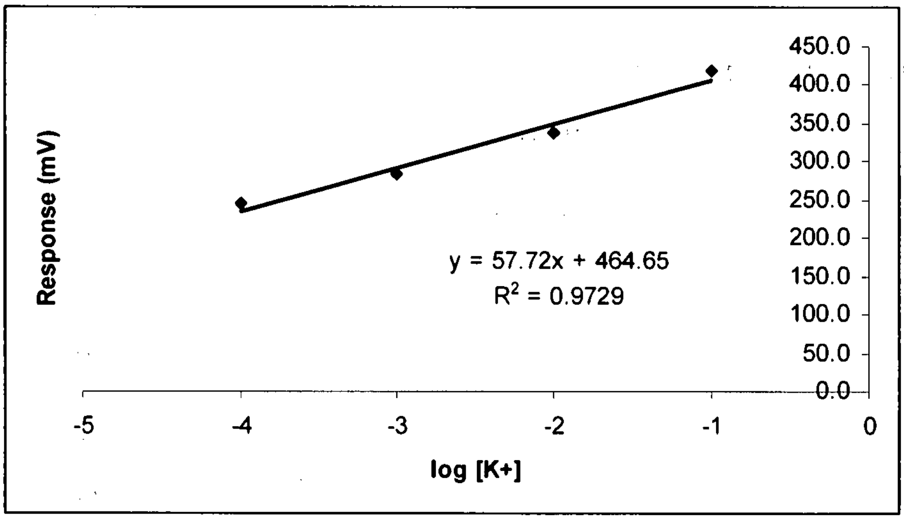


Figure 4