

OPTIMIZATION OF SCREEN PRINTED REFERENCE ELECTRODE BASED ON CHARGE BALANCE AND POLY (BUTYL ACRYLATE) PHOTOCURABLE MEBRANE

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Abstract

This research focus on transforming the traditional design of reference electrode into all-solid-state reference electrode front-end using Ag/AgCl screen- printed electrodes. By replacing the internal reference solution of a traditional reference electrode by a solid photocurable membrane, an all-solid-state reference electrode can be achieved. The solid-state screen-printed reference electrode was designed using a photocurable acrylic film containing immobilized sodium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB) and trimethyloctylammonium chloride (TOMA-Cl). An optimum ratio of NaTFPB:TOMA-Cl = 1:1 produced a stable reference electrode. In the anions interference studies, all anions i.e. NO₃⁻, Cl⁻, Br⁻ and SO₄²⁻ does not give effect to the SPRE except perchlorate anions. The all-solid-state reference electrodes was applied to the detection of potassium ions and ammonium ions. Validation of the all-screen-printed reference electrode was performed with reference electrode standard gel type. The validation results showed that all-solid-state screen-printed reference electrode demonstrated performance that was comparable to standard reference electrode.

Keywords: Reference Electrode, Screen Printed Electrode, Poly(Butyl Acrylate), Photocurable Membrane

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1. Introduction

Potentiometry method is one of the methods that is very interesting in many applications for the measurement of the ion with the wide linear range. This is because the potentiometric electrodes can be designed with portable platform, disposable and tool is also not expensive. This analysis technique in particular is widely applied for medical and environmental applications [1]. Thick and thin film technology used to produce the corresponding sensor or disposable equipment. One type of disposable sensor that is screen printed electrode (SPE). The technology of making this electrode is not expensive and can be generated in large quantities [2-3].

One of the most important components in the potentiometry method is reference electrode. At this time, the reference electrodes that are present in the marketplace are mostly large size, and then it will be perceived difficult when formed into single package which disposable electrode pair [4-7]. Therefore, the loss of attention to the research of miniaturization of the reference electrode can be a barrier in measurement technology development with the

potentiometry method. This is imputable to the sensor on the potentiometry methods has produced with rapid to affect to the screen printed electrode technology. Hence the reference electrodes from the potentiometric sensors should also act towards the same [8]. In electrochemistry system, the reference electrode functions to specify the potential energy of the electrochemical cell by means of comparison with electrode work. And then that the potential energy reference electrode must be secured, stable and not impressed by the changes in the concentrations of the samples [9-10].

Several researchers in decades have tried to do miniaturization of reference electrode. Hyuk et al. report on the design of reference electrode without using the liquid salt bridge. In his research, Hyuk et al. using a membrane polymer poly (urethane) (PU) containing two types of lipophilic such as potassium tetrakis (p-chlorophenyl) borate (KTPClPB) and tridodecyl methyl ammonium chloride (TDMA-Cl) [11]. Other than Hyuk et al, other researchers are Simonis et al reported the printing layer of Ag/AgCl on the surface of a silicon substrate, followed by

coating the surface of the Ag/AgCl by using agar gel-containing KCl salt, and then a layer of Agar gel/KCl protected by a membrane of poly (vinyl chloride)/cellulose nitrate (PVC/SN) [12]. Meanwhile, Anna et al. successfully designing a planar-shaped reference electrode using PVC membrane which containing potassium tetrakis (4-chlorophenyl) borate (KTpCIPB) and also tridodecyl methyl ammonium chloride (TDMA-Cl) in the ratio 1:1. In addition, PVC is used coupled with an aliquot consisting rather than a mixture of KCl: AgCl with a proportion of 5: 1 to maintain the stability of its potency. [13].

The research itself aims to study and design a reference electrode in the form of solid-state, two-dimensional and small-sized and can be fabricated in screen printed technology. This reference electrode can be used in measurements involving ion selective sensor. One of the challenges in this research is how to use reference electrode that require salt bridge liquid to the solid electrode without a liquid salt bridge, a small planar shape, and membrane used are not easily damaged. If the reference electrode membrane is damaged, it will cause a change in the concentration of the electrolyte in the reference electrode. This contributes to potential instability reference electrode, wherein the potential value Ag/AgCl on the reference electrode will change with the concentration of the electrolyte [10,12].

Studies which carried out using a membrane of poly (butyl acrylate) which contains both types of lipophilic such as sodium tetrakis [bis-3,5 (trifluoromethyl) phenyl] borate (NaTFPB) and also trioctyl methyl ammonium chloride (TOMA-Cl).

2. Experimental and Procedures

2.1 Materials

Chemicals used in this study are n-butyl acrylate (nBA 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPP 99%), 1,6-hexanediol diacrylate (HDDA 99%) from Sigma Aldrich, sodium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate (NaTFPB) and trioctylmethyl ammonium chloride (TOMA-Cl) from Fluka, KCl 99.5% , KNO₃ 99.5% and also KBr 99.5% from Merck, K₂SO₄ 99.5% from Riedel-deHaen, KClO₄ 99% from BDH, NH₄Cl 99.5 % from Ajax, and DI water.

2.2 Experiment

Ag/AgCl SPE electrodes from Screen Print Sdn. Bhd. are used for the fabrication of electrode potentiometric. On the top layer of Ag/AgCl SPE electrodes coated with a mixture containing n-butyl

acrylate monomer, 0.1 wt% cross-linker agent 1,6-hexanediol diacrylate and 2 wt% photoinitiator 2,2-dimethoxy-2-phenylacetophenone, sodium tetrakis [bis-3,5 (trifluoromethyl) phenyl] borate and trioctylmethyl ammonium chloride with mole ratio variation. The next, photo polymerization carried out for three minutes using an ultraviolet light exposure tool (RS Ltd.) under atmospheric nitrogen. After the fabrication process is completed, then examining the performance of a screen printed reference electrode (SPRE) of Ag/AgCl.

3. Results and Discussion

3.1 The Effect of Lipophilic Salts Ratio

Screen printed electrode (SPRE) without salt bridge liquid in the design using a membrane of poly (n-butyl acrylate) with a mole ratio that is the same for both lipophilic salts is sodium tetrakis [bis-3,5 (trifluoromethyl) phenyl] borate (NaTFPB) and trioctylmethyl ammonium chloride (TOMA-Cl). Poly (n-butyl acrylate) was selected as the material for the membrane because in screen printed technology, the membrane used must have a high adhesive strength on several types of substrates[1, 14]. In addition, the polymer of poly (n-butyl acrylate) having the characteristics do not require plasticizers and hydrophobic. [15-19].

In the fabrication of the planar sensor, the adhesiveness of membrane on the surface of the sensor is one of the elements that influence the lifetime and also the stability of the sensor [9]. Membrane materials used should also have microcavity and serve as a bridge between the inner electrolyte salt and sample [20-21]. The overall features of the membrane are filled with poly (n-butyl acrylate). This is really different from the polyvinyl chloride (PVC), because it requires the plasticizer to lower the electrical impedance.

The amount of salt lipophilic was used with certain ratios. Lipophilic salt used is usually consists of a rich material with a negative charge such as potassium tetrakis (p-chlorophenyl) borate (KTpCIPB) and also materials that are rich in positive charges like tridodecylmethyl ammonium chloride (TDMA-Cl). The materials used must be in an equal amount so that the number of net charges in the membrane is empty and then the electrode potential energy does not vary with the modification in the boot on the ion solution or sensitivity to almost not exist [11]. In this study, some of the compositions of sodium tetrakis [bis-3,5 (trifluoromethyl) phenyl] borate (NaTFPB) and trioctyl methyl ammonium chloride (TOMA-Cl) as

shown in Table 1 are used together to create a state of charge balance in the membrane electrode.

Table 1. Composition of the additional material lipophilic cations and anions present in the membrane electrode type of poly (n-butyl acrylate)

No Membran	NaTFPB (mole)	TOMA-Cl(mole)	Ratio	Potential Different (ΔmV)
1	-	6.53×10^{-3}	-	69.60 ± 1.05
2	3.38×10^{-7}	3.46×10^{-7}	1:1	5.30 ± 0.12
3	1.75×10^{-7}	3.00×10^{-7}	1:2	48.60 ± 1.12
4	1.24×10^{-6}	1.24×10^{-6}	1:1	58.70 ± 0.85
5	4.00×10^{-7}	4.00×10^{-7}	1:1	6.40 ± 0.25
6	6.00×10^{-7}	6.00×10^{-7}	1:1	10.30 ± 0.15
7	1.74×10^{-7}	9.00×10^{-7}	1:5	110.50 ± 0.71

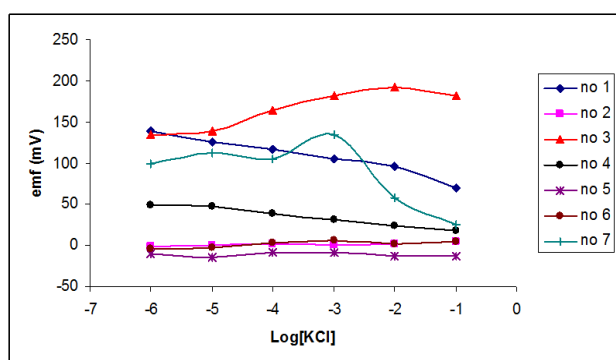


Fig. 1. Response of the solid state reference electrode based on membrane poly (n-butyl acrylate) membrane containing with variations of composition TOMA-Cl and NaTFPB

Fig. 1 demonstrates the result of the ratio of the quantity of additional material cations and anions to the electrode on the reaction of solids. Membrane number 1 provided only using TOMA-Cl, the response shown is a negative. In fact, that TOMA-Cl will improve the distribution of positive charges on the membrane surface of poly (n-butyl acrylate), and this will further facilitate ion Cl^- to introduce into the membrane, so that it will provide a stimulus to the negative charge [22].

In the membrane No. 2 and 5, the response is more stable, i.e. ΔmV 5.30 ± 0.12 and 6.40 ± 0.25 . The content of lipophilic ionic additives is almost equal in the membrane 2 and 5. The amount of net charge practically not exists on the surface of the film because the charge is contrary as though experiencing a neutralizing each other. This condition causes no sensitivity to the nature of the ions in solution. Due to limited lipophilic ionic additives is balanced and it gives influence to a number of charges in the surface of the film to cancel each other [11,23-25].

However, membrane No. 2 is better than the membrane No. 5 for use as a reference electrode. It appears at the membrane No. 2 gives smaller potential differences and stable [9-10].

Meanwhile membranes No. 4 and 6, although both have a proportion of 1:1, but the value is greater potential energy difference compared to membrane No. 2 and 5. This is imputable to the amount of lipophilic ions used are also getting larger, and the distribution of positive and negative charges in the membrane also getting. The pull of anions and cations to move faster and more into the membrane phase and this will affect the potential value of analyte concentration when changes take place [11]. In the membrane No. 3 and 7, the value of the potential energy difference found is more outstanding. This is influenced by the amount of the ratio of the two lipophilic ions unbalanced. The more unbalanced number of moles of the lipophilic ionic, differences in potential energy generated is also greater [10-11, 23-25].

3.2 Stability Study

One of the most important things in designing screen printed reference electrode (SPRE) is screen printed stability. The main factor that may give effect to the potential energy stability properties of SPRE is:

- i. Direct contact between the sample with the surface layer of Ag/AgCl. This occurs if the electrode used is leaking, so the disruption of anion especially Cl^- , causing changes in the potential value of the SPRE [10,12].
- ii. Dissolving of the AgCl material into the sample solution. This seldom applies to SPRE or a solid electrode. Dissolution of AgCl material effect on the ordinary reference electrode bridged type of liquid salt. Nevertheless, if the SPRE too often hit it up too long will also speed up the process of

dissolution of AgCl from Ag/AgCl. In solution, AgCl be able to produce ions Cl^- follow reaction $\text{AgCl} + e \longrightarrow \text{Ag}^+ + \text{Cl}^-$, so that balance and concentration of Cl^- changing, and could affect the value of the potential from reference electrode [13,23-24].

iii. Properties of the membrane used. In the fabrication of a solid-state reference electrode, the membranes play a role to facilitate the movement of ions from the sample towards reference electrode. If the material used is too hydrophilic, it will cause the solution move into the membrane and the membrane will be pulled out from the surface of the electrode. Otherwise, if highly hydrophobic membranes used, This may lead to bottlenecks in the movement of ions in the membrane and electrode may disturb the potential value of the SPRE fabricated [11,25].

In this study, the stability of the reference electrode was determined by measuring the change in the potential value of four different KCl concentrations are 1 M, 0.1 M, 10⁻³ M and 10⁻⁶ M. Measurement of the potential value of all the KCl solution was performed at every hour for seven hours. Fig. 2 shows the stability patterns of SPRE with the measurement time. For the first five hours, the potential value changes in the range of 0.97 ± 0.04 mV/dec and have a RSD of 3.95%. After that, the reference electrode potential value increased by more than 10 mV. Such a situation is probably caused by problems with a lipophilic salt component in the membrane were expelled, causing the charge in the membrane becomes unbalanced [11,21]. This finally makes the reference electrode is sensitive to modifications in the content of ions in the samples.

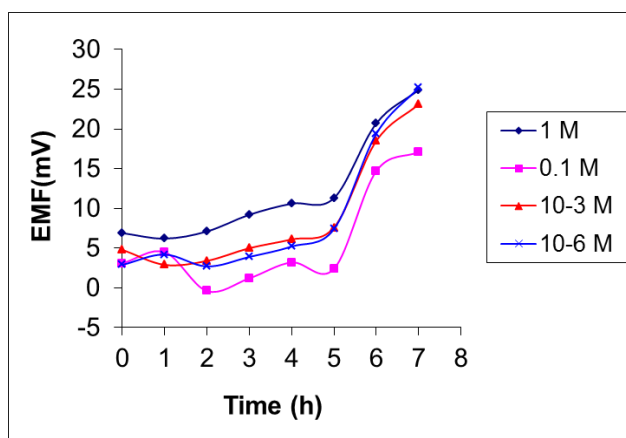


Fig.2. Stability of the SPRE based on a membrane which contains lipophilic ion NaTFPB and TOMA-Cl at various concentrations of KCl

3.3 Anions Effect

In this study, TOMA-Cl is used as a material to increase conductivity in the membrane layer. TOMA-Cl is an organic cation having a high lipophilicity. TOMA-Cl presence will cause the membrane to have a positive charge and this will cause the anions to interact with it in the ion exchange process [22]. Therefore, it needs to run a study to determine whether anions may provide interference effects on performance of SPRE that has been fabricated.

Anions used in the interference study are Cl^- , NO_3^- , Br^- , SO_4^{2-} , and ClO_4^- with a concentration of 0.1 M to 10⁻⁸ M. In this interference study, SPRE functioned as a working electrode. The potential value measured is referenced to a standard reference electrode gel type. The result of the presence of some inorganic anions can be viewed in Fig. 3.

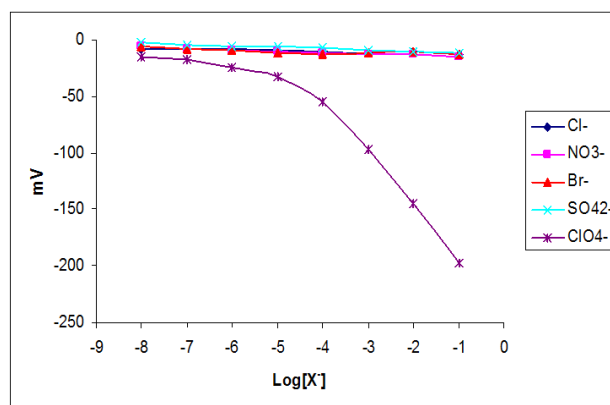


Fig.3. Effect presence of some of the anions on the SPRE

All anions studied does not give effect to the SPRE except perchlorate anions that cause the clear interference. The value of the potential difference (ΔmV) for each anion can be seen in Table 2.

Table 2. Value potential difference (ΔmV) some anions to SPRE using NaTFPB and TOMA-Cl.

Anion	ΔmV	R.S.D (%), n = 3
Cl^-	5.40 ± 0.31	5.62
NO_3^-	8.40 ± 0.21	2.49
Br^-	8.00 ± 0.51	6.39
SO_4^{2-}	9.00 ± 0.40	4.47
ClO_4^-	173.20 ± 9.08	5.24

The effect of interference by perchlorate anion are caused by the constant increase in dielectric membrane containing ionic lipophilic. In Hofmeisters series, namely grouping ion based on its ability to change the structure in the water,

perchlorate ions have the properties of lipophilicity a more stronger compared to NO_3^- , Cl^- , Br^- and SO_4^{2-} ions, thus it is really easy for perchlorate ions to extract into the membrane phase and this will provide interference in reference electrode [10,26].

3.4 Applications of SPRE as a Reference Electrode for Ion Sensor

The aim of this work was to test whether the reference electrode created to be able used with ion sensor. Testing is performed by measuring the response and performance of sensors potassium ion sensors and ammonium ion sensors. The outcomes of the work compared to the responses of both types of sensors are obtained from measurements using standard reference electrode gel. Response and performance ion sensor obtained are presented in Fig. 4 and Table 3.

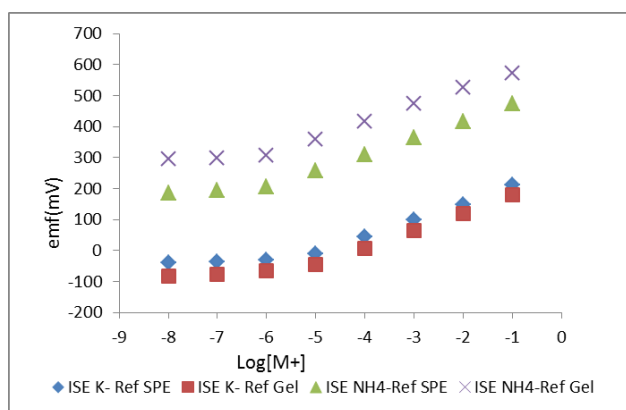


Fig.4. Comparison Performance Ion Sensor with SPRE and standard reference electrode gel

Table 3. Comparability of the performance of potassium and ammonium ion sensor using a SPRE and a reference electrode gel standard.

Sen sor	RE	Linear Range (M)	Slope (mV/dec)	LOD (M)
K^+	SP	$0.1 - 10^{-5}$	54.10 ± 0.60	$(3.35 \pm 0.64) \times 10^{-6}$
	RE Gel	$0.1 - 10^{-5}$	56.10 ± 0.17	$(2.70 \pm 0.29) \times 10^{-6}$
NH_4^+	SP	$0.1 - 10^{-6}$	52.10 ± 1.35	$(4.92 \pm 0.92) \times 10^{-7}$
	RE Gel	$0.1 - 10^{-6}$	55.40 ± 1.04	$(6.73 \pm 1.54) \times 10^{-7}$

Fig. 4 and Table 3 shows the measurement results are not so different between both sensors involving SPRE and standard reference electrode gel. This is confirmed by the results of the t-test with a confidence level of 95%, where the value of the t-

test indicated potassium ion sensor is 0.005, and ammonium ions is 0.03. Overall slope the measurement closely with Nernstian value is 59.16 mV/dec. Nevertheless, it was found that the slope sensor uses SPRE are lower compared with the measurement standard reference electrode gel. This is likely made by the absence of an inner layer from SPRE which may stabilize overloaded as found in reference electrode Ag/AgCl double junction. This term can affect and degrade the stability [10,12].

4. Conclusions

Reference electrodes were prepared in this study has a planar configuration and the type of electrode Ag/AgCl. The membranes used comprised of a single layer of photopolymer poly (butyl acrylate) containing two types of ion lipophilic ie NaTFPB and TOMA-Cl. The presence of both lipophilic ions with the same ratio has resulted in membrane electrode is not affected by changes in ion in solution. This is able produce a reference electrode that has a potential value of a fixed and stable in the state of various concentrations of samples. The study also found that the SPRE reference electrode provides performance analysis is similar to a standard reference electrode gel when used together with potassium and ammonium ion sensor

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