

SCREEN-PRINTED POTASSIUM ION SENSOR FABRICATED FROM PHOTOCURABLE AND SELF- PLASTICIZED ACRYLIC FILM

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Abstract: *Potassium ion sensor based on photocured poly(n-butyl acrylate) membrane has been fabricated on screen printed electrode (SPE) through a photocuring technique. The advantage of the fabrication method allows miniaturized but two-dimensional sensor that is disposable to be designed. The potassium ion sensor yielded a Nernstian response, i.e., 58.5 ± 0.5 mV/decade when the potassium ion concentrations were 10^{-1} – 10^{-5} M. The limit of detection was close to $(2.5 \pm 0.57) \times 10^{-6}$ M. The potassium ion SPE also demonstrated little interference from cations such as Ca^{2+} , Mg^{2+} , Li^{+} , and Na^{+} and good reproducibility with relative standard error of 0.81% ($n = 4$). The sensors were applied to the analysis of potassium in urine and the results were compared with that of a conventional technique such as flame photometry.*

Keywords: Potassium ion sensor, plasticizer free acrylic membrane, urine analysis, Ag/AgCl screen-printed electrode, photopolymerization

1. INTRODUCTION

Potassium ion sensors have many biomedical applications. They are used in the analysis of blood, and urine potassium and cardiovascular research and monitoring. Obviously, in cardiovascular applications the use of miniaturized ion-selective sensor is desirable, thus requiring microfabrication of the sensor [1]. The most common ion-selective-electrode construction requires an ion-selective membrane of a polymeric type containing ionophore [2]. Poly(vinyl chloride) (PVC) is conventionally used as a membrane matrix. However PVC gave many problems when used in fabricating solid-state sensor. This is because PVC membrane has poor adhesion on solid substrate, can only be prepared from solvent casting procedure [1,3,4] and requires a plasticizer for the purpose of softening the polymer [5]. Many of the problems encountered by PVC membrane can be resolved by the use of photocurable and self-plasticizing polymer matrix based on acrylic polymers. The idea of a self-plasticizing membrane for ion-selective sensor was developed recently where the acrylic membrane material has been shown to yield functional ion sensors without the incorporation of

plasticizer [1,2,5–8]. A number of potentiometric [9,10] and optical ion [11] sensors were developed and shown to give similar performance to conventional ion-selective electrodes based on plasticized PVC membranes.

Cross-linked poly(*n*-butyl acrylate) (PBA) was proven as a useful membrane material for ion sensor. The main advantages of PBA are its good adhesion, photocurable and self-plasticizing properties because the glass transition temperature of polymer is close to -30°C . The non-requirement of plasticizer and good adhesion property allow successful deposition of membrane on solid surface, and this enables application in solid-state ion sensors [2, 12].

Recently, electrodes prepared from screen printed technology or screen-printed electrodes (SPE) have been popular and many electrode used in electrochemical sensors, particularly for amperometry are SPEs. SPEs are prepared mainly by thick-film process via screen-printing of the electrode design with suitable inks onto a planar substrate material by forcing the ink through a patterned stencil or mask. This is then followed by thermal curing. A wide range of inks and substrate materials can be used in the manufacturing of SPEs. Commercial carbon and metal (Pt or Au) ink formulations are commonly used for printing the working electrodes, whereas silver based inks are used for obtaining the reference electrode and also as working electrode for ion-selective electrodes [13]. SPEs have been used in many sensor applications [4,12–15]. The popularity of the technology in fabricating electrode is attributed to the simple production method that enables mass production of electrode strip at low cost. The SPEs can be made disposable, miniaturized [4,12–13] and with potential in fabricating sensor arrays [14].

In this study, the characteristics and application of potassium ion sensors that based on PBA membrane fabricated by photocurable technique on Ag/AgCl SPEs are investigated. The compatibility of the PBA membrane with the SPE for potassium ion sensing is demonstrated.

2. RESEARCH METHODOLOGY

2.1. Reagents

Membrane materials such as *n*-butyl acrylate, 2-hexenedioldiacrylate and 2,2-dimethoxyl-2-phenylacetopenone, 2-hydroxyethyl methacrylate were purchased from Sigma. Valinomycin, sodium tetrakis[bis-3,5(trifluoromethyl)phenyl] borate, lithium acetate dehydrate, tris(hydroxymethyl) aminomethane (Tris), chlorides of potassium, ammonium,

sodium, calcium and lithium (all are analytical grade) were from Fluka. Standard solutions were prepared in deionized water.

2.2. Sensor Fabrication

The SPE (Scrint Print Ltd. Malaysia) consists of printed layers Ag/AgCl on Silver tracks and a feature that allow the entrapment of membrane cocktails before photocuring. The inner layer of the sensor was fabricated from the monomer of 2-hydroxyethyl methacrylate with 1.6 wt.% of the photoinitiator 2,2-dimethoxyl-2-phenylacetopenone, which was first deposited on the Ag/AgCl SPE. The mixture was photocured under UV radiation in an UV-exposure unit (RS Ltd, UK) under constant flow of nitrogen gas for 3 min. After photocuring, this polymer layer (pHEMA) was hydrated with 0.01 M potassium chloride solution for 10 min to form the inner layer of the sensor.

The self-plasticizing poly(*n*-butyl acrylate) film was then deposited on top of hydrated pHEMA inner layer by depositing a cocktail that contained the monomer *n*-butyl acrylate, 0.1 wt.% of cross linker 2-hexenedioldiacrylate and 2 wt.% of photoinitiator 2,2-dimethoxyl-2-phenylacetopenone, 3.8 wt.% of valinomycin ionophore and 24 mol% (relative to the ionophore) of sodium tetrakis[bis-3,5(trifluoromethyl)phenyl] borate followed by photocuring in an UV-exposure unit (RS Ltd. UK) under constant flow of nitrogen gas for 3 min [9]. For comparison purposes, rod shape Ag/AgCl electrodes of length 3 cm and diameter 2 mm (Warner USA) were used with the ion sensing membrane deposited as that describe in the fabrication of potassium ion SPE.

2.3. Sensor Characteristic Evaluation

The response of all sensors were assessed in an electrochemical cell setup, which consisted of double junction Ag/AgCl reference electrode as reported by Heng and Hall [2]. The internal reference solution was 0.1 M Tris-HCl (pH = 7) whilst 0.1 M lithium acetate was used as a gel bridge electrolyte. Both the reference electrode and the potassium sensor were connected to an Orion ion meter. The difference in the potential of the cell or electromotive force (emf) in mV was recorded when a stable value was reached, which is normally 2–5 min [5]. Interference study was carried out by the separated solution method (SSM) [16] with 0.1 M chloride solutions of the interference cations of ammonium, sodium, calcium, magnesium and lithium. Reproducibility of the SPEs was assessed using four different sensors fabricated from the same batch.

The potassium SPEs were evaluated in terms of application to potassium ion analysis in urine samples. Three undiluted urine samples were tested by three

different potassium SPEs fabricated from the same batch. The reproducibility of the analysis was also examined. In order to compare the potassium content determined by the potassium sensors with that of other established methods, a flame photometer was used to analyze the potassium content of the undiluted urine samples.

3 RESULT AND DISCUSSION

Potentiometry is based on the electrochemical phenomenon expressed by the Nernst equation where the logarithmic of the activity or concentration of the ions is proportional to the difference in the potentiometric cell potential measured at a fixed temperature [17]. Nernstian response occurs when an ion-selective electrode response according to "local" thermodynamic equilibrium, was determined over a given range of activity (or concentration). Nernstian slope can be obtained from a plot of the potential difference of the ISE cell versus the logarithm of the ionic activity of a given species. A Nernstian response is obtained when such a plot is linear with a slope 59.16 mV per unit charge of p_{A} at 298.15 K [16].

Valinomycin ionophore in the membrane can selectively form a complex potassium ion from the solution [18,19]. The complexation process from the membrane-solution interface allows transfer of the potassium ion into the non-plasticized membrane and this causes the overall change of potential of the sensor in response to change of potassium ion concentration. In a membrane with no plasticizer such as that of PBA, potassium ion is suggested to move through the membrane by an ion "hopping" mechanism [20].

3.1. Sensitivity and Selectivity of Potassium Ion SPEs

Table 1 shows the linear response obtained for four different screen-printed sensors (from the same batch of fabrication) towards various potassium ion concentrations in the range of 0.1 to 10^{-5} M. The sensitivity was almost near Nernstian, i.e., close to 58.5 ± 0.5 mV/decade ($n = 4$) (Fig. 1). The response of the potassium ion SPEs was found to be similar to potassium ion sensor prepared from Ag/AgCl rod shape electrodes (Table 1). In terms of interference by other major cations, the potassium ion SPEs demonstrated good selectivity towards potassium ion in the presence of the other major cations such as sodium, lithium, calcium and magnesium (Table 2). The sensor response is affected by the 0.1 M ammonium ions. According to a few researchers [5,23,24], the presence of ammonium ions might strongly interfered with the sensor response, thus resulting in severe competition between potassium and ammonium cations for complex formation in the membrane phase. Other SPEs reported using different

types of ionophores or polymer matrices demonstrated selectivity coefficients for potassium ions in the presence of sodium ions ranged from -0.2 to -2.9 whilst for ammonium ion -1.4 [25–28].

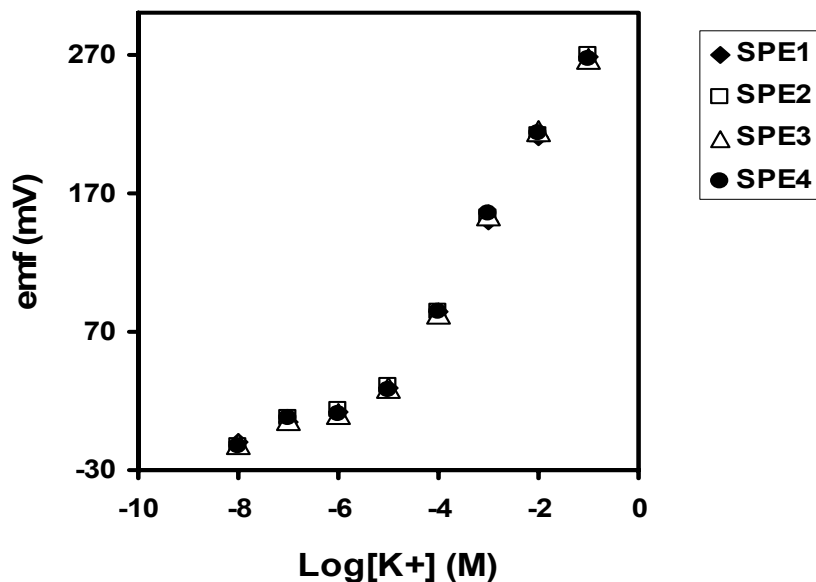


Figure 1: The response of four potassium ion sensors fabricated based on photocured self-plasticizing membrane and SPE towards change of potassium ion concentrations

Table 1: The analytical performance of the potassium ion sensor based on photocured self-plasticizing acrylic membranes and screen-printed electrodes

Sensor	Slope (mV/decade)	Linear range (M)	r^2	Detection limit (10^{-6} M)
SPE 1	58.4	10^{-1} to 10^{-5}	0.9985	2.5
SPE 2	58.3	10^{-1} to 10^{-5}	0.9986	3.2
SPE 3	58.2	10^{-1} to 10^{-5}	0.9978	2.5
SPE 4	59.2	10^{-1} to 10^{-5}	0.9979	1.6
Rod Ag/AgCl	58.6	10^{-1} to 10^{-6}	0.9964	0.02

Table 2: The selectivity behaviour ($\text{Log } K_{K,B}^{\text{pot}}$) of the potassium ion sensors with self-plasticizing membranes in the presence of 0.1 M of various cations

Interference cation	$\text{Log } K_{K,B}^{\text{pot}}$ (SPE)	$\text{Log } K_{K,B}^{\text{pot}}$ (Rod)
NH_4^+	-1.39	-1.23
Na^+	-2.99	-2.84
Ca^{2+}	-4.59	-4.83
Mg^{2+}	-4.52	-4.69
Li^+	-4.27	-4.32

Similar selectivity pattern was obtained for potassium ion sensors prepared from rod shape Ag/AgCl electrodes with the same formulation of the membrane matrix (Table 2). In general, the response behaviour in terms of both sensitivity and selectivity of the potassium ion SPEs is similar to that of solid-state electrodes prepared by using non-screen printing technique such as conventional solid Ag/AgCl electrodes. Furthermore, the response of the potassium ion SPEs from this is in close agreement with many other studies using non-screen printed electrode [9,21,22].

All potassium ion SPEs demonstrated detection limits in the range of 10^{-6} M and this is about 100 times higher than that observed in potassium ion sensor based on rod shape Ag/AgCl electrode. However, the limit of detection, which is close to 10^{-6} M is similar to many other non screen-printed potassium ion-selective electrodes reported previously [7,9,21]. The detection limit of an ion-selective electrode can be improved by changing the composition of the inner solution so that the concentration of the analyte ion is low. This might lead to influx of the ions from the sample side to the inner solution, thus lowering the detection limit [5]. For solid-state potassium ion sensor where the inner layer is a solid rather than a solution, e.g., the hydrated pHEMA layer in the potassium SPE of this study, it is not known how such mechanism can operate to lower the detection limit of the sensor.

Potassium ion SPEs was found to have good reproducibility with standard relative error of not exceeding 0.81% ($n = 4$). This shows that SPE as a substrate for ion sensor design does not affect the behaviour of the ion-sensing membrane. The good stability of the sensor is attributed to the good adhesion property of the PBA film, which allows good contact between the SPE substrate and the sensing membrane.

3.1.1 Application of Potassium Ion SPEs For The Analysis of Human Urine

The potassium ion SPEs were used to analyze the potassium ion content of three different undiluted human urine samples that contained different concentrations of potassium (Table 3). The potassium content of the urine samples is similar to those analyzed by the flame photometric method, but with better reproducibility of RSD < 5% when compared with the flame method. The concentrations of potassium ion also correlated well with data obtained from flame photometric method ($[K^+]_{\text{flame}} = 1.1609 [K^+]_{\text{SPE}} - 0.3586$, $r^2 = 0.9961$, $n = 9$). This indicated that there was no major interference for potassium ion analysis from urine sample matrix using the potassium ion SPEs, although the sample is expected to contain ammonium ions normally not exceeding 10^{-3} M[29]. At this low concentration of ammonium, the interference on potassium ion detection is not obvious.

Table 3: A comparison of potassium ion determined in urine samples by potassium ion SPEs and flame photometer

Urine samples	K ⁺ content (mM)	K ⁺ content (mM)
	SPE method (n = 3)	Flame method (n = 3)
Sample 1	14.27 ± 0.33	15.30 ± 1.52
Sample 2	3.72 ± 0.16	3.89 ± 1.52
Sample 3	24.74 ± 0.47	26.70 ± 2.53

4. CONCLUSION

Photocurable and self-plasticized poly(n-butyl acrylate) membrane on screen-sprinted Ag/AgCl electrode could produce potassium sensor of equally good analytical performance to that of other conventional design of potassium ion selective-electrodes, solid-state or otherwise. The sensor mass production is at low cost, thus enabling the sensor to be used as a disposable device, which is an important requirement in clinical samples analysis such as urine, blood and other body fluids.

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