POTASSIUM ION SELECTIVE ELECTRODE USING POLYANILINE AND MATRIX-SUPPORTED ION-SELECTIVE PVC MEMBRANE

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Abstract — Solid-state potassium ion selective electrode (K⁺ ISE) has been the most studied chemical sensors due to its practical importance in biomedical applications. One of the major obstacles that prevented widespread use of solid-state K⁺ ISE has been output potential drift problem. In this report, we developed an electrochemical sensing unit which working, counter and reference electrodes are integrated in a single plane as all-solid-state form. In order to mitigate the output potential drift, a polyaniline intermediate layer and salt-saturated polyvinylebutyral top coating are introduced in the working and reference electrodes, respectively. Using cyclic voltammetry (CV), uniform layers of polyaniline are deposited on carbon electrode, as confirmed by scanning electron microscope (SEM) observation. Potentiometry and electrochemical impedance spectroscopy (EIS) measurement on our K⁺ ISE show high sensitivity (60.5 mV/decade), low concentration for the limit of detection ($10^{-5}$ M), and large range of linear detection ($10^5 – 1$ M), and superior selectivity of K⁺ ISE against NH⁺, Na⁺, Mg²⁺, Ca²⁺, and Fe³⁺. With its high potential to be miniaturized, we foresee that our solid-state K⁺ ISE will motivate future applications in microdevices for clinical analysis, agricultural and, environmental applications.

Index Terms — Solid-state ion selective electrode, Potassium sensor, Potentiometry, Signal stability

I. INTRODUCTION

Wearable devices for health monitoring create new opportunities for personalized remote healthcare in recent years [1]. Chemical homeostasis is one of the most important subjects for sensors. Among chemicals, potassium ions have critical importance for all levels of vital activities [2]. In fact, potassium monitoring in food and serum [3], urine [4], and potentially in brain [5] has been a routine analysis in the clinical and medical fields to reveal physical conditions of the patients having renal diseases, hypopotassemia, alkalosis, cirrhosis of liver, or using diuretic drugs [6]. Thus, miniaturized K⁺ sensor is highly demanded for wearable health monitoring system.

Conventional K⁺ sensing methods include flame photometry [7-9], ion chromatography [10], surface plasmon resonance [11], and electrochemical detection [12]. Among these technologies, electrochemical ion-selective electrode (ISE) has many advantages including fabrication simplicity, high selectivity towards a specific ion, fast response time, wide linear range, reproducibility and potential for miniaturization [13]. Using solid-state ISEs without internal filling solution provides a durable, flexible and portable ion sensor that can easily be miniaturized.

Ionophores, complex molecules that allow permeation of the K⁺ ions while block others, is the key material for solid-state ion selective electrodes. The discovery of ionophore for K⁺ detection was based on biological research which revealed that valinomycin, a dodecadepsipeptide antibiotic which can be isolated from Streptomyces, possesses an internal cavity whose size matches closely with the diameter of K⁺ [14]. This means that valinomycin can easily form ionic bonds with K⁺. Other ions, for example Na⁺, whose diameter is significantly smaller than the pore, cannot form a complex together; the selectivity for K⁺ over Na⁺ is over 1000 times [15-17]. The mobility of ionophore and lipophilic counterions in the ion selective membrane significantly affect the frequency of interaction of K⁺ and ionophore at the polymer/solution interface, which is important for the functionality of ISE. Due to concentration gradient, K⁺ that formed ionic bonding with ionophores are mobile inside the liquid phase (plasticizer) of ion selective membrane, while other species are blocked outside. In rigid polyvinyl chloride (PVC), diffusion coefficient was in range of $10^{-6}$ cm²/s for small gas molecules such as H₂ and He, and up to $10^{-7}$ cm²/s for CCl₄, let alone bulky organic molecules such as valinomycin [18]. Hence, adding plasticizer to PVC membrane

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is necessary to promote diffusion process of ionophore and to equilibrate the chemical potential more quickly. This way, response time is shortened. Diffusion coefficient of valinomycin through membrane consisting of about 33% PVC - bis(2-ethylhexyl) sebacate (DOS) is in the order of $10^{-8}$ cm$^2$/s [19].

Figure 1a illustrates the mechanism that causes the issue of potential instability when the ion selective membrane is in direct contact with the electron-conducting substrate. According to the Nernst equation, membrane potential changes logarithmically to $K^+$ ions activity; this can only be true when $[K^+]$ transduces to the electric potential without any delay or loss [20]. Here, water layer at the interface between the ion selective membrane and electrically conducting substrate damps out capacitive junction and as a result, no transition from ions to electrons [14]. In 2000, it has been proved that a thin water layer between Au and ion selective membrane is responsible for the potential drift and such problem can be reduced by depositing a lipophillic monolayer, such as thiol compounds, on top of the metal contact [21]. Alternatively, conducting polymer between the electronic conductor and the ion-selective membrane to give high potential stability but does not influence the analytical performance of ISE including selectivity, sensitivity, and limit of detection [20]. Over the past few years, conducting polymers have been applied as promising ion-to-electron transducers for solid contact ISEs because they exhibit both electrical and ionic conductivity which means they can help ion-to-electron transition by oxidation/reduction of conducting polymers (Figure 1b) [22, 23]. Many electronically conducting polymers including polypyrroles [24], poly(3-octylthiophene) (POT) [25], and poly(3,4-ethylenedioxythiophene) (PEDOT) [26], and polyaniline (PANI) [27] were tested as ion-to-electron transducers. It should be noted that PANI does not prevent water layer formation; rather, its conductivity is stable over a wide range of water content [28, 29]. Therefore, in this study, PANI was chosen due to its high conductivity in presence of water ($10^{-3} – 10^{-2}$ S/cm) and facile synthesis.

With an emergence of flexible and wearable bioelectronics, there has been a revival of ion selective electrodes in the last few years owing to its potential to miniaturization. This novel application requires a complete integrated system of ISE and reference electrode. Most of the recent studies solely focus on the modifications of WE while the effect of RE modification is less frequently studied (see Table 1 and references therein). In fact, the stability of miniaturized RE has been a longstanding issue for potentiometric measurements using solid-state electrodes [21, 30]. The purpose of a RE is to provide a stable potential that is independent with surrounding sample. The major issue of solid-state Ag/AgCl RE was the leakage of inorganic salt [31]. In this study, we employed the NaCl-saturated PVB membrane to prevent the leakage of AgCl; the aim of our work was to come up with a simple method to fabricate a $K^+$ ISE with high selectivity and stable sensitivity. We applied a commercial screen-printed electrode (SPE) with an extra intermediate layer (polyaniline) to solve the potential drift problem. Additionally, the miniaturized reference electrode (Ag/AgCl) was placed on the same plane as working and was modified by polyvinyl butyral (PVB) and sodium chloride layer to maintain constant concentration of chloride ions and prevent leaking of silver chloride. Finally, our $K^+$ ISE exhibits good selectivity ($-\log K_{K^+ Na^+} = 4.36$), high sensitivity (60.5mV/decade), low concentration for the limit of detection ($10^{-5.8}$ M), large range of linear detection ($10^{-5} – 1$ M), and potential stability (up to 12 hours) high concentration of NaCl mimics the salt bridge, thus the output stability was further enhanced.

![Fig. 1. Schematics that describe: (a) the water layer that forms between the ion selective membrane and electronically conducting substrate and (b) how an electrochemically transducing intermediate layer, such as polyaniline (PANI), mitigates the adverse effect by the water layer.](image-url)
Table 1. Summary of recent studies of solid-state potassium ion selective electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Intermediate layer/ Ionophore</th>
<th>Reference</th>
<th>Selectivity ((-\log K_{K^+, Na^+}))</th>
<th>Sensitivity ((\text{mV/decade}))</th>
<th>LOD ((10^n \text{ M}))</th>
<th>Linear range ((\text{M}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>N/A / valinomycin</td>
<td>SCE</td>
<td>N/A</td>
<td>49</td>
<td>5</td>
<td>(10^{-3} - 10^{-1})</td>
<td>[32]</td>
</tr>
<tr>
<td>Pt</td>
<td>Ppy / calixarene</td>
<td>N/A</td>
<td>N/A</td>
<td>51</td>
<td>5.7</td>
<td>(10^{-3.2} - 10^{-1})</td>
<td>[33]</td>
</tr>
<tr>
<td>Pt</td>
<td>PANI / dbdb-18-6</td>
<td>SCE</td>
<td>2.5</td>
<td>58</td>
<td>5.8</td>
<td>(10^{-3} - 10^{-1})</td>
<td>[34]</td>
</tr>
<tr>
<td>Au</td>
<td>PEDOT-PSS / valinomycin</td>
<td>Ag/AgCl/3 M KCl</td>
<td>3</td>
<td>61.3</td>
<td>3</td>
<td>(10^{-1} - 10^{-5})</td>
<td>[35]</td>
</tr>
<tr>
<td>GC</td>
<td>Graphene / valinomycin</td>
<td>N/A</td>
<td>N/A</td>
<td>58.4</td>
<td>6.2</td>
<td>(10^{-5.8} - 10^{-1})</td>
<td>[36]</td>
</tr>
<tr>
<td>Graphite</td>
<td>Mixture of CB, poly(amidoacid) Cu(I) complex, resin / valinomycin</td>
<td>Ag/AgCl/3.5 M KCl</td>
<td>N/A</td>
<td>59</td>
<td>7</td>
<td>(10^{-6} - 10^{-1})</td>
<td>[37]</td>
</tr>
<tr>
<td>Cu</td>
<td>Graphite-epoxy-hardener / valinomycin</td>
<td>Solid Ag/AgCl</td>
<td>4.11</td>
<td>44</td>
<td>4.4</td>
<td>(10^{-4.3} - 10^{-1})</td>
<td>[38]</td>
</tr>
<tr>
<td>Ag</td>
<td>N/A / PBE</td>
<td>Ag/AgCl/3 M KCl</td>
<td>1.3</td>
<td>56.3</td>
<td>4.7</td>
<td>(10^{-4} - 10^{-1})</td>
<td>[39]</td>
</tr>
<tr>
<td>GC</td>
<td>Hexanethiolate monolayer protected gold cluster / valinomycin</td>
<td>Ag/AgCl/3 M KCl</td>
<td>N/A</td>
<td>57.4</td>
<td>6.1</td>
<td>(10^{-3} - 10^{-1})</td>
<td>[40]</td>
</tr>
<tr>
<td>Pt</td>
<td>Ppy and zeolite / valinomycin</td>
<td>Ag/AgCl/3 M KCl</td>
<td>N/A</td>
<td>54.2</td>
<td>5.1</td>
<td>(10^{-3} - 10^{-2})</td>
<td>[12]</td>
</tr>
<tr>
<td>GC</td>
<td>MoO₂ / valinomycin</td>
<td>Ag/AgCl/3 M KCl</td>
<td>N/A</td>
<td>55</td>
<td>5.5</td>
<td>(10^{-3} - 10^{-3})</td>
<td>[41]</td>
</tr>
<tr>
<td>Carbon SPE</td>
<td>PANI / valinomycin</td>
<td>Modified solid Ag/AgCl</td>
<td>4.36</td>
<td>60.5</td>
<td>5.8</td>
<td>(10^{-3} - 1)</td>
<td>This work</td>
</tr>
</tbody>
</table>

LOD: limit of detection; GC: glassy carbon; N/A: not available; SCE: saturated calomel electrode; Pt: platinum; Ppy: polypyrrole; PANI: polyaniline; dbdb-8-6: 4′,4″(5″)-di-tert-butyldibenzo-18-crown-6-ether; PEDOT-PSS: poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; CB: carbon black; PBE: poly(benzyl eugenol); SPE: screen-printed electrode
II. MATERIALS AND METHODS

2.1. Materials and Instruments

Aniline, potassium ionophore I (Valinomycin), potassium tetrakis(4-chlorophenyl)borate (KTPCB), bis(2-ethylhexyl) sebacate (DOS), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), potassium chloride (KCl), sodium chloride (NaCl), polyvinyl butyral (PVB, Butvar® B-98), methanol (CH₃OH), ammonium chloride (NH₄Cl) and iron(III) chloride (FeCl₃) were purchased from Sigma-Aldrich. Hydrochloric acid was purchased from Caledon Laboratories Ltd. Magnesium chloride (MgCl₂) and calcium chloride (CaCl₂) were purchased from Fisher Scientific. All the chemicals were of analytical grade and used as received without further purification. Artificial blood serum (pH 7.4) was prepared by adding 0.05 mM NH₄Cl, 130 mM NaCl, 0.8 MgCl₂, and 1.4 mM CaCl₂ in de-ionized water (DIW).

Morphology of polyaniline was observed by field-emission scanning electron microscope (Zeiss EVO MA10, Jena, Germany). Electrochemical measurements were carried out with AUTOLAB potentiostat/galvanostat (PGSTAT302N, Metrohm Autolab B.V., Utrecht, The Netherlands). Commercial screen-printed electrodes (DRP 150, DropSense, S.L., Llanera, Spain) containing a carbon working electrode (diameter: 4 mm), a solid Ag/AgCl reference electrode and a platinum counter electrode were used to prepare K⁺ ISE. All the experiments were conducted at room temperature (20°C).

2.2. PANI polymerization

Carbon working electrode on SPE was coated with PANI by using cyclic voltammetry from 0 to 1 V vs. Ag/AgCl with scan rate of 100 mV/s in 0.03 M aniline and 0.05 M HCl. The process was repeated 30 cycles and stopped at 1 V. Here, we denote the PANI coated SPE as SPE/PANI. After that, SPE/PANI was dried in oven for 30 mins at 110°C. Similarly, response of K⁺ ISE was measured in artificial serum with spiked KCl between 10⁻⁵ and 1 M.

Potential stability measurements

Potential was performed for SPE/PANI/V with and without PANI layer as described in the experimental section by using CV. Here, we adopted the CV method for PANI deposition because it allows a more homogeneous deposition [42]. We found that 30 cycles allowed the best result for PANI layer quality, in terms of the balance between thickness and adhesion. Figure 3 shows the morphological contrast between SPE and SPE/PANI. Here, we confirmed that the 30 CV cycles

2.4. Electromotive force measurements (EMF)

Prepared electrodes (SPE/V and SPE/PANI/V) were conditioned in 0.01 M KCl solution for 2 h prior to use. The selectivity factors were determined by separate solution method to measure EMF of different solutions of K⁺, NH₄⁺, Na⁺, Mg²⁺, Fe³⁺ at the same activity (0.1 M).

Sensitivity of K⁺ ISE was determined by measuring in diluted KCl solution through 8 concentration steps (1, 10⁻¹, 10⁻², 10⁻³, 10⁻⁴, 10⁻⁵, 10⁻⁶ M KCl). After measuring the electrode in a solution for 120 seconds, the electrode was quickly cleaned with DIW and immersed in the next solution. Similarly, response of K⁺ ISE was measured in artificial serum with spiked KCl between 10⁻⁵ and 1 M.

2.5. Electrochemical impedance spectroscopy (EIS)

EIS was measured with SPE/V, SPE/PANI/V and SPE/PANI/V without modified reference electrode. Impedance spectra were recorded in the frequency range 100 kHz to 10 mHz at the open circuit potential in 0.1 M KCl. The modulation amplitude used was 10 mV. Data was fitted based on the equivalent circuit models in ZSimpWin software to elucidate electrochemical process between the interface of solution and electrode.

2.6. Potential stability measurements

Potential was performed for SPE/PANI/V with and without PVB/NaCl layer on reference electrode in 0.1 M of KCl for 12 hours.

III. RESULTS AND DISCUSSION

3.1. Characterization of polyaniline

In general, electrochemical polymerisation of aniline can be carried out by using one of the three techniques: (i) potentiostatic method (applying a constant voltage), (ii) cyclic voltammetry (CV), and (iii) galvanostatic method (applying a constant current) to an aqueous solution of aniline. PANI was deposited on WE as described in the experimental section by using CV. Here, we adopted the CV method for PANI deposition because it allows a more homogeneous deposition [42]. We found that 30 cycles allowed the best result for PANI layer quality, in terms of the balance between thickness and adhesion. Figure 3 shows the morphological contrast between SPE and SPE/PANI. Here, we confirmed that the 30 CV cycles
allow well-distributed granular PANI homogeneously deposited on the carbon electrode.

![SEM images showing morphology of (a) SPE (the bare carbon working electrode) and (b) SPE/PANI (PANI deposited on carbon working electrode by 30 CV cycles).](Image)

Figure 3. SEM images showing morphology of (a) SPE (the bare carbon working electrode) and (b) SPE/PANI (PANI deposited on carbon working electrode by 30 CV cycles).

Figure 4a shows the polymerization of aniline in 0.5 M HCl. The wide oxidation peak in the first cycle at 0.8 V vs. Ag/AgCl reflects the nucleation of aniline onto the site of carbon. After the first scan, this oxidation peak decreases and well-defined new peaks at 0.2 and 0.35 V indicate the growth of PANI film [43]. After the polymerization step, electrode was inserted into a solution of 0.1 M KCl to evaluate the quality of the formed polymer layer. In Figure 4b, the redox peaks at 0.130 and 0.370 are assigned to the reduction of partly oxidized emeraldine (electrically conducting) to the reduced form leucoemeraldine (electrically insulating) and vise versa. The produced PANI varies with oxidation states ranging from leucoemeraldine (fully reduced), emeraldine (half oxidized), and pernigraniline (fully oxidized) [44]. The CV result in Fig 4a indicates that some portion of the produced PANI is leucoemeraldine, which has the worst electrical conductivity among PANI (10⁻¹⁰ – 10⁻⁸ S/cm) states. Fortunately, leucoemeraldine is very unstable and can easily be converted to emeraldine salt, which is electrically conducting (10⁻² – 10⁻¹ S/cm), when dipped in an acidic medium [45, 46].

![Cyclic voltammetry (CV) spectra that were obtained (a) during the deposition of PANI in 0.5 M HCl (30 cycles overlapped; red line shows the first scan) and (b) after the 30-cycle deposition of PANI in 0.1 M KCl for quality evaluation (third scan). Here in (b), the spectrum from pure SPE was also overlaid for comparison.](Image)

Fig. 4. Cyclic voltammetry (CV) spectra that were obtained (a) during the deposition of PANI in 0.5 M HCl (30 cycles overlapped; red line shows the first scan) and (b) after the 30-cycle deposition of PANI in 0.1 M KCl for quality evaluation (third scan). Here in (b), the spectrum from pure SPE was also overlaid for comparison.

Figure 5a shows a Nyquist plot from EIS measurements of bare SPE and SPE/PANI in 0.1 M KCl solution with a modulation amplitude of 10 mV and the corresponding simulation results in line. Here, the imaginary axis for bare SPE is nearly perpendicular with real axis. Thus, the spectrum of the bare SPE can be fitted to a series circuit of solution resistance (Rₛ) and double layer capacitance (Cₐ). On the other hand, that the spectrum of SPE/PANI inclines outward. In this case, a series of solution resistance (Rₛ), a constant phase element (CPE), and Warburg impedance (Zₗ). CPE is a fitting parameter in electrochemical impedance measurements to represent an imperfect capacitor. There are many factors that causes a CPE such as surface roughness, varying thickness or pore size distribution across electrode surface resulting in inhomogeneous reaction rate [47, 48]. The adoption of CPE in the equivalent circuit for SPE/PANI is reasonable because PANI deposited on electrode surface increases electrode surface roughness and homogeneity.

![Electrochemical impedance spectroscopy (EIS) spectrum at high frequency of WE before and after aniline polymerization in 0.1 M KCl. Dot results were obtained from experiments while straight line represented fitting data from ZSimpWin. Inset plot shows full EIS spectrum. (b) The two equivalent circuits to fit SPE (top) and SPE/PANI (bottom).](Image)

Fig. 5. (a) Electrochemical impedance spectroscopy (EIS) spectrum at high frequency of WE before and after aniline polymerization in 0.1 M KCl. Dot results were obtained from experiments while straight line represented fitting data from ZSimpWin. Inset plot shows full EIS spectrum. (b) The two equivalent circuits to fit SPE (top) and SPE/PANI (bottom).

3.2. Selectivity test

Selectivity coefficient Kᵢⱼₘₗ one of the most important parameter to determine the quality of an ISE. The selectivity is determined by combination of ionophore and other electrode membrane components. Here, Nernst equation for real solutions presenting ion of interest i and interfering species j is:

\[ E = E^0 + \frac{RT}{z_i F} \ln \left( a_i \ + \ \sum K_{ij}^{pot}(a_j)^{z_j/z_i} \right) \]  

(1)

with E: electrode potential, E₀: standard electrode potential, R: gas constant, T: absolute temperature, z: valence of the ion, F: Faraday constant, and a: activity of the ion.

In our study, we employed a separate solution method to
measure selectivity coefficient $K_{ij}^{pot}$ [49]. The potential of SPE/PANI/V is measured with separate solutions of cations at the same activity (0.1 M). If the measured values are $E_i$ and $E_j$ for $K^+$ and other interferents, respectively, the value of $K_{ij}^{pot}$ may be calculated from the equation:

$$\log K_{ij}^{pot} = \frac{(E_j - E_i) z_i F}{RT \ln 10} + \left(1 - \frac{z_i}{z_j}\right) \log a_i$$

(2)

As shown in Figure 6, $K_{ij}^{pot}$ was obtained for mono-, di- and trivalent cations. $NH_4^+$ can interfere the most with $K^+$ detection because $NH_4^+$ has a similar value of hydrated ionic radius as $K^+$ ion. In case of biomedical applications such as analyzing human’s interstitial fluid, $Na^+$ and $K^+$ are of the most concern. Here, $[Na^+]$ typically varies between 145 – 155 mM while $K^+$ level fluctuates between 3.5 – 5.5 mM [50]. Our sensing electrode displayed $K_{ij}^{pot}$ value of $Na^+$ over $K^+$ to be about $4.32 \times 10^{-5}$, meaning it takes more than 23,000 $Na^+$ ions to modulate the electrode potential as one $K^+$ ion does. Therefore, the selectivity of our electrode is adequate to apply in analyzing human’s interstitial fluid.

![Figure 6. Response of $K^+$ ISE for different cations at the same activity (0.1 M). (a) Potential values from potentiometry measurement and (b) selectivity coefficient $K_{ij}^{pot}$ calculated from (a).](image)

3.3. Sensitivity test

Figure 7a shows the potential output between the working and the reference electrodes when SPE/V and SPE/PANI/V were employed as working electrodes, respectively, with respect to time immersed in the KCl solution with varying ionic concentration. The figure also evidences that the inclusion of PANI interlayer remarkably reduces the potential drift. Constructing a calibration curve (i.e. reploting the average potential values against $[K^+]$) in Figure 7b shows that SPE/V and SPE/PANI/V have a linear range from $10^{-4}$ to 1 M and $10^{-5}$ to 1 M of KCl, respectively. As a result, detection limit was improved from $10^{-4.3}$ M (SPE/V) to $10^{-5.8}$ M (SPE/PANI/V) of KCl, and sensitivity increased from 52.3 ± 3.1 mV/decade (SPE/V) to 60.5 ± 5.3 mV/decade (SPE/PANI/V).

![Figure 7. (a) Electromotive force (EMF) measurements recorded for decreasing concentration of $K^+$ in DIW, (b) average calibration curve ($N = 3$).](image)

3.4. EIS

In this part, EIS measurements were fitted to the equivalent circuit (Figure 8b) representing solution resistance ($R_s$), charge transfer resistance ($R_{ct}$) at the membrane/solution interface, CPE and the finite-length Warburg impedance ($Z_W$). As mentioned before, CPE was used instead of capacitor for better agreement with the measurement. We intended to make observation whether there is a qualitative difference between the three differently modified electrodes, SPE/V, SPE/PANI/V, and SPE/PANI/V with PVB modified reference electrodes. As can be seen in Figure 8a, smaller semicircle indicates the reduction in charge transfer resistance of SPE/PANI/V compared to SPE/V. In addition, the PVB modification on RE did not impact the characteristics of $K^+$ ISE.

![Figure 8. (a) Impedance measurements between SPE/V, SPE/PANI/V (with as-received reference electrode), and SPE/PANI/V with PVB modified reference electrode. (b)](image)
The equivalent circuit used for simulations to fit the measured EIS spectra.

3.5. Artificial serum test

Ion fluxes are highly regulated across human cell membrane by specific ion channels; especially crucial for signaling in nerve and muscle cells are \( K^+ \) of which intracellular and extracellular concentration exhibit the utmost level of selective control between 130 – 150 and 3.5 – 5.5 mM, respectively [51-53]. Any disequilibrium implies neuronal diseases (i.e. epilepsy) or nephrosis (i.e. renal failure), where \( K^+ \) concentration in extracellular space reaches up to 10 mM may cause a stroke [34, 53]. Extracellular fluids (blood plasma and interstitial fluid) contains various analytes from cations, anions, organic acids and proteins. Figure 9 has shown that, in artificial blood serum, \( K^+ \) ISE still gives a good linear result covering from \( 10^{-3} \) to 1 M with 54.8 ± 1.2 mV/decade, and detection limit of \( 10^{-5} \) M of KCl, which is well below the normal level in human extracellular fluids.

![Fig. 9. (a) EMF measurements recorded for decreasing concentration of K+ in artificial serum, (b) average calibration curve (N = 3).](image)

3.6. Potential stability

This test is carried out to evaluate the stability of \( K^+ \) ISE when reference electrode is covered with PVB/NaCl layer. Solid Ag/AgCl reference is unstable due to delamination of AgCl salt in aqueous solution. As shown in Figure 10, potential drift of \( K^+ \) electrode vs. Ag/AgCl was calculated by measuring the slope of potential in the first 3 hours to be 1.17 \( \mu \)V/s, followed by severe instability. On the other hand, the potential drift of \( K^+ \) electrode vs. modified Ag/AgCl was 0.78 \( \mu \)V/s in 12 hours, while the signal stayed stable and consistent over the entire duration of the measurement. Therefore, PVB/NaCl membrane has proved to prevent leaking of AgCl.

![Fig. 10. EMF measurements in 0.1 M KCl of K+ ISE with and without PVB/NaCl layer on reference electrode.](image)

IV. CONCLUSION

In this study, PANI has proved to enhance the performance of potassium sensor whose sensitivity was 60.5 mV/decade. Limit of detection for potassium ions was \( 10^{-5.8} \) M. In addition, modified solid Ag/AgCl reference prolongs the stability of output potential. PANI based potassium ion selective electrodes and PVB/NaCl coated reference electrodes have been tested in artificial serum. The demonstrated high sensitivity, short-term stability and all-in-one solid-state setup may add another stepping stone towards biomedical applications for monitoring the concentration of \( K^+ \) in important healthcare applications, such as blood, plasma, serum, sweat in future studies.

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REFERENCES


