

Ag/AgCl Film Electrodes Coated with Agarose Gel as Planar Reference Electrodes for Potentiometric Sensors

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Abstract Silver/silver chloride (Ag/AgCl) is commonly used as a reference electrode in electrochemical measurements. However, commercial macroscopic Ag/AgCl electrodes cannot be used in micro-electrochemical sensors. Thus, many scientists are trying to miniaturize reference electrodes to integrate into one sensor chip. In this paper a new approach for fabrication of Ag/AgCl thin films coated with agarose gel as planar reference electrodes for potentiometric sensors is introduced. A silver thin film of 220-250 nm was sputtered and patterned on silicon dioxide/silicon substrates by lithography and lift-off techniques. A AgCl layer was coated on the Ag film by using a $\text{Ag}[\text{NH}_3]_2\text{Cl}$ complex at 80°C in vacuum. The thickness of the AgCl layers was about 5 μm . The Ag/AgCl layers were then coated with an agarose gel. The AgCl layers were characterized by X-ray diffraction, micro Raman spectroscopy and scanning electron microscopy. The Open Circuit Potential (OCP) measurements with the fabricated electrodes as reference electrodes in pH 7 buffer solutions were performed in comparison with a commercial Ag/AgCl electrode. The potential difference between the fabricated Ag/AgCl electrodes and the commercial Ag/AgCl electrode was insignificant. The coating of the agarose layer as a protection layer of the Ag/AgCl electrodes enhanced the durability of the modified electrodes. The results indicated that the fabricated Ag/AgCl thin films coated with the agarose gel could be used as planar reference electrodes for potentiometric sensors.

Keywords Ag/AgCl, Reference Electrode, $\text{Ag}(\text{NH}_3)_2\text{Cl}$ Complex, Agarose

1. Introduction

Silver/silver chloride (Ag/AgCl) is often used as material of a reference electrode, which is used popularly in electrochemical measurements. However, conventional Ag/AgCl electrodes are normally in macro-scale which

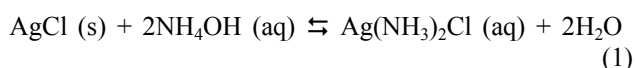
cannot be employed in micro-electrochemical sensors [1]. Thus, many scientists are trying to minimize and integrate the reference electrode with the other sensors on a chip for biomedical and environmental applications [1-6].

A conventional Ag/AgCl electrode is constructed by a silver wire coated with AgCl. This Ag/AgCl wire is then embedded into a liquid electrolyte of saturated KCl. To fabricate a Ag/AgCl micro-electrode, the electrode should be re-designed to a solid state instead. There are some methods to fabricate a solid state Ag/AgCl electrode such as thin film deposition, electrochemical coating, screen printing. For example, Suzuki et al. fabricated a Ag/AgCl thin film electrode by sputtering 300 nm silver layer and a AgCl layer was grown from the silver pattern by chronopotentiometric method at a constant current of 20 μA [7] or Kim et al. deposited 1,000 nm silver layer on a glass substrate using radio frequency sputtering and direct-current sputtering technique and chlorinated the Ag layer with a drop of FeCl_3 50 mM [8]. Likewise Huang et al. sputtered an Ag layer with 4 μm thickness on a Si/SiO₂ wafer and then chlorinated by electrochemical method in 0.1 M HCl at a constant voltage of 1.0 V [9]. Electrochemical method was also applied with other chlorine solution such as KCl, NaCl, ... at different currents and potentials to grow the silver chloride layer on the silver backbone [4, 6, 10, 11]. However, the electrochemical deposition might apply well only for an electrode with a thickness of a few micrometers because the chlorination causes the silver layer corroded rapidly. Deposition of a thick layer is not an advantage of the sputtering technique which is often used in nano-scaled thin films. Some studies prefer screen printing method. They could fabricate a quasi-reference electrode Ag/AgCl without protecting layer or all-solid-state reference electrode Ag/AgCl/electrolyte/protecting layer simply by printing the components of electrode step by step. For instance, Zielińska et al. [12] printed an ion-selective chloride electrode on a polyester foil content of silver contact, carbon layer and insulating layer. After each printing step, the layer of ink was cured at different conditions like heating or UV irradiation. Liao et al. also printed a solid

state planar Ag/AgCl electrode by screen printing with a silver paste, but the AgCl layer was formed by immersing the silver electrode in a FeCl₃ solution 1 M for 1 minute then the KCl agarose gel electrolyte was smeared on the Ag/AgCl sequentially [13]. Idegami et al. [14] and Cranny et al. [15] used a paste of Ag/AgCl mixture as a printing ink and used other kinds of paste and gel for printing the solid electrolyte and protection layer. The screen printing technique is an easy way to make a micro-scaled Ag/AgCl electrode. However, the printed layers usually have the thickness ranging from several hundreds micrometers to some millimeters. In addition, with this technique, many components are required for the paste formula, which results in less purity of the printed electrode.

Bare Ag/AgCl electrodes are easily degraded in solutions during electrochemical measurements. Therefore, protection layers are often coated on top of the Ag/AgCl electrodes to increase durability. In some studies, the surface of Ag/AgCl electrodes was covered with a polymeric electrolyte [16, 17]. Besides, Nafion [18, 19] or a metallic layer [20] could be used to protect the Ag/AgCl thin film in planar reference electrodes. Agarose gel has been used as an electrolyte layer in combination with chloroprene rubber to form a protection layer of the Ag/AgCl electrodes [13, 21].

In this study, a new approach was used to fabricate Ag/AgCl thin films for planar reference electrodes. A AgCl thin layer was deposited on the sputtered Ag layer surface by drop coating. A complex of Ag(NH₃)₂Cl was used to deposit the AgCl layer. Thanks to high solubility of this complex in water, the solution could be drop-coated easily. Furthermore, the complex had reversibility so it could be returned to the salt form - AgCl by slightly heating. The reactions of composition and decomposition of the Ag(NH₃)₂Cl complex are shown as Eq. 1 and Eq. 2 below.



The AgCl layer reformed from the decomposition of the Ag(NH₃)₂Cl complex easily covered the surface of the Ag electrode. Moreover, less contamination was caused because the decomposition produced the vapor gas as in Eq. 2. Finally, the Ag/AgCl electrode layer was covered by a layer of agarose gel.

2. Materials and Methods

2.1. Materials

Acetone, iso-propanol and ethanol were purchased from Merck, Germany. Ma-P1215 positive photoresist, hexamethyldisilazane (HMDS) and ma-MF_320 developer solution were purchased from Micro Resist, Germany.

Silver nitrate (AgNO₃) 99% was purchased from Scharlab S.L., Spain. Sulfuric acid (H₂SO₄) 98%,

hydrogen peroxide (H₂O₂) 30%, sodium chloride (NaCl), ammoniac solution (NH₃) 25% and potassium chloride (KCl) were purchased from Xilong, China. Agarose powder 100% was purchased from Vietxo Co., Vietnam. Deionized (DI) water was supplied by a DI system (Purelab Ultra, Elga Co., UK), the resistance of the outlet water was 18.2 MOhms. The pH buffer solutions from Hanna Instruments Vietnam were used as electrolyte in the electrochemical measurements.

2.2. Fabrication of the Ag Planar Electrodes

The Ag electrodes were fabricated with dimension as shown in **Fig. 1**. The Ag electrodes were fabricated on the (100) silicon wafers (Okmetic, Finland) with 4 inch diameter, 380 μm thickness, the surface resistance of approximately 5-10 Ω.cm. The wafers were washed with piranha solution (mixture of 15 ml H₂SO₄ 98% and 5 ml H₂O₂ 30%), DI water, acetone and iso-propanol. After cleaning, a SiO₂ insulator layer with 700 nm thickness was coated on the silicon wafer by the oxidation furnace PEO 601 (ATV, Germany). After that, the Si/SiO₂ wafer was washed with piranha solution, DI water, acetone and iso-propanol respectively for 5 minutes.

The photolithography process was used for fabrication of the Ag planar electrodes. The Ti and Ag layers were sputtered by the sputtering system Univex 350 (Leybold, Germany). The Ti layer with a few nanometers was used as an adhesive layer between the wafer Si/SiO₂ and the Ag layer on the top.

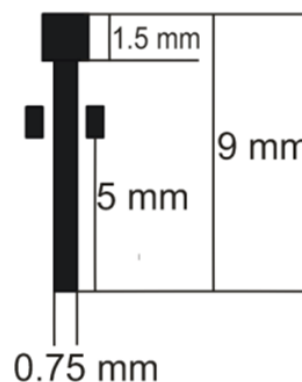


Figure 1. Dimension of a silver electrode

2.3. Coating AgCl on the Ag Electrode

1 ml AgNO₃ 0.2 M solution was mixed with 1 ml NaCl 0.3 M solution to produce precipitated AgCl. This salt was rinsed at least 5 times, each time with 10 ml of DI water to eliminate the residual reactants. After rinsing step, 170 μl NH₃ 25% solution was added to dissolve AgCl and subsequently form a soluble Ag(NH₃)₂Cl complex. Finally, the Ag(NH₃)₂Cl complex was distilled in DI water with total volume of 1.7 ml to produce 0.021 g/ml concentration of the complex.

4 μl of the distilled complex solution was dropped on the fabricated Ag electrode. Then the Ag electrode with

the complex drop was heated at 80°C for 5 minutes in a vacuum oven. Dropping manipulation was repeated once more on the same position and then heated at 80°C in vacuum for 30 minutes. **Fig. 2** shows the Ag/AgCl electrode before and after AgCl coating.

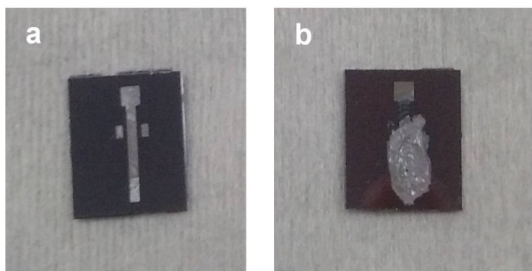


Figure 2. The photos of the Ag electrode before (a) and after (b) coated with the AgCl layer.

2.4. Coating Agarose Layer on the Ag/AgCl Electrode

The agarose solution 2% was prepared by diluting 0.2 g agarose powder in 10 ml DI water at 80°C. The solution was stirred for 10 - 15 minutes until agarose powder was completely dissolved in the solution. 5 μ l of the agarose solution was dropped on the surface of the Ag/AgCl electrode and left at room temperature for 24 hours to stabilize. **Fig. 3** shows the Ag/AgCl/agarose electrode before and after drying.

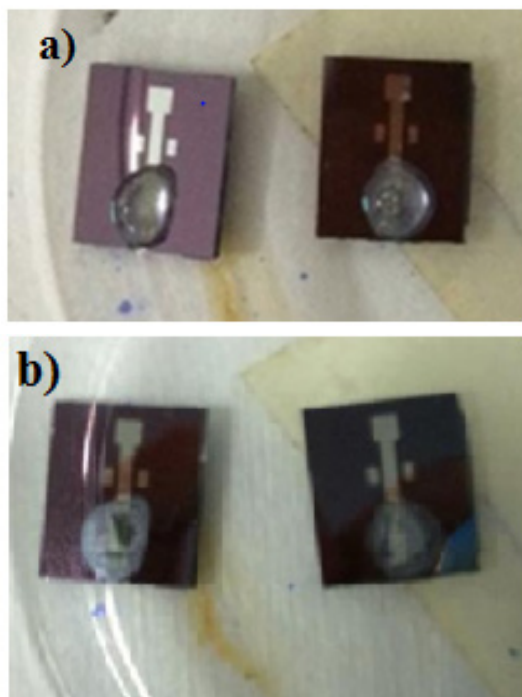


Figure 3. The photos of the Ag|AgCl|Agarose electrodes before (a) and after (b) drying.

2.5. Characterization

Thickness of the Ag/AgCl electrodes was measured by a stylus profiler Dektak 6M (Veeco, USA) and Scanning Electron Microscopy - SEM (JSM-6480LV, Jeol, Japan). Structural characterization of Ag/AgCl was performed by X-Ray diffraction (XRD) on Diffraktometer D500 (Siemens, Germany), Energy dispersive X-ray spectroscopy (EDS) integrated in the FE-SEM S4800 (Hitachi, Japan), Micro Raman spectroscopy on Lab RAM 300 (Jobin Yvon, France).

Thickness of the Ag/AgCl/agarose layer was measured by the stylus profiler Dektak 6M (Veeco, USA). Physical stability and durability of the Ag/AgCl/agarose layer was tested by immersing the fabricated electrodes in DI water and pH 7 buffer solution for various periods (from 2- 24 hours).

2.6. Electrochemical Characterization

The fabricated Ag/AgCl electrodes and the Ag/AgCl/agarose electrodes were used to measure the Open Circuit Potential (OCP) vs. the commercial Ag/AgCl reference electrode (Basi Inc., US) and the potential of the electrodes in the pH 7 buffer solution was measured with the Autolab PGSTAT-302N, Metrohm, the Netherlands. The measurement time was 300 seconds and the dE/dt limit was 10^{-6} . The measurement would be stopped when the change of the potential over time reached 10^{-6} . During the measurement time, there was no current through the electrochemical cell.

For the Ag/AgCl electrodes, the OCP measurement was performed for 3 times. The Ag/AgCl/agarose electrode's OCP measurement was performed for 8 times in 2 weeks.

3. Results and Discussion

3.1. Characterization of the Fabricated Ag/AgCl Electrodes

The thickness of the Ag and AgCl layers was measured by Dektak 6M. The thickness of the Ag layer was 187 ± 20 nm, and the thickness of the Ag/AgCl layer was $4,689 \pm 278$ nm. The result was in good accordance with the observation of the SEM images on the cross section of the Ag/AgCl layer (Fig. 4). The SEM image showed that the Ag/AgCl layer was formed quite uniformly and the thickness was about 5 μ m.

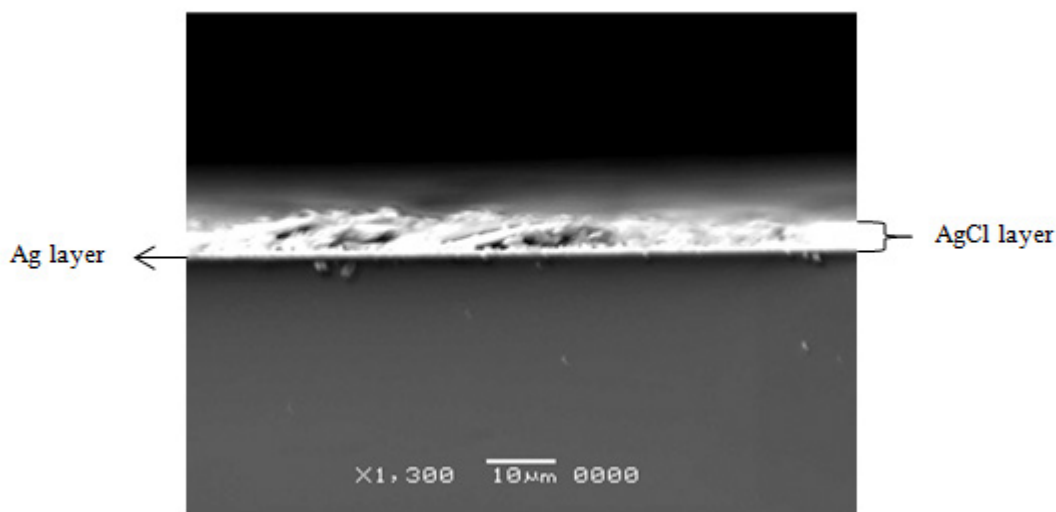


Figure 4. The SEM image on the cross section of the Ag/AgCl layer.

The formation of AgCl was determined by XRD which exhibited the specific diffraction peaks of AgCl (Fig. 5). Unlike the other reports, the XRD of AgCl formed by decomposition of $\text{Ag}(\text{NH}_3)_2\text{Cl}$ had a highest peak at $2\theta = 28^\circ$ (111) instead of 32° (200). This revealed that the AgCl crystal might not exist in nanosphere as in synthesis of Hu et al. [22] or nanocubic structure of Yang et al. [23] or the others of nanoparticle [24] but with another morphology. The crystallization of the AgCl mainly followed by the development of planar (111) implied that the AgCl crystal might be grown from the vertices of an original cubic to construct a branch type of crystal as described by Lou [25] and Tian [26]. Because the AgCl crystallized from the $\text{Ag}(\text{NH}_3)_2\text{Cl}$ complex without inhibition of any solvent or surfactant, crystallization had enough time to rebuild the lattice gradually and was not suspended. As a result, crystallization constructed a micro-branched crystal with the low surface energy of -0.273 Jm^{-3} of the AgCl (111) facets [25].

On the other hand, the Ag peak did not appear in the XRD spectrum, it could be due to the huge difference in thickness between Ag layer and AgCl layer. The thickness of AgCl layer was 40 times thicker than the thickness of the Ag layer, so the peak of Ag layer could not appear in the XRD spectrum.

The EDS analysis (Fig. 6) indicated the peaks of the elements present in the sample, which are in good agreement with the reported EDS results [16]. In the EDS results, there were mainly Ag and Cl in the sample, the molar ratio of Ag:AgCl was 1:1.3. The residual contaminants from the complex such as N, H were not present. Nevertheless, there was a small content of Si and O which were from the SiO_2 substrate. The EDS results showed that the AgCl was produced with high purity.

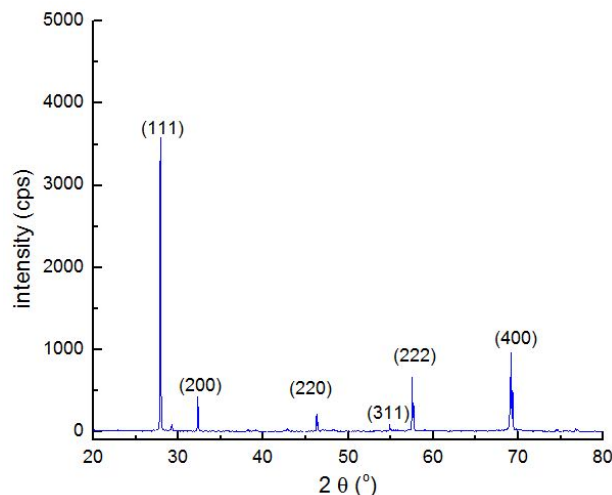


Figure 5. The XRD of the AgCl layer formed on the Ag layer.

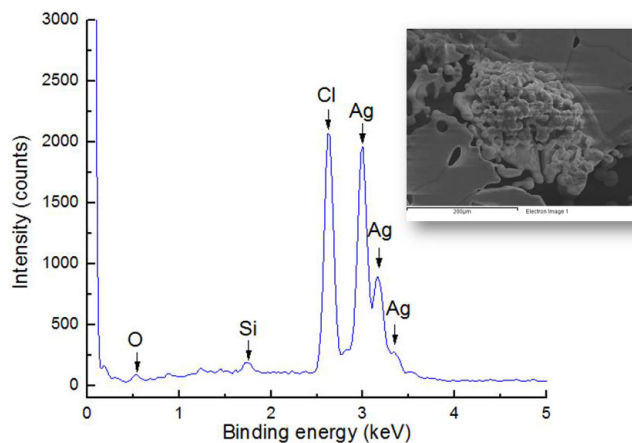


Figure 6. The EDS spectrum of the Ag electrode coated with the AgCl layer.

To consolidate the above results, the Raman spectrum of the Ag/AgCl electrode was performed (**Fig 6**). There was a good accordance in Raman shift with other reported results [27]. For instance, the vibration of the Ag lattice and the stretching of Ag-Cl bond could be found at the Raman shift of 99, 135, 225 cm^{-1} corresponding to 95, 143, 233 cm^{-1} of the ref. [27]. It could be concluded that the AgCl layer was formed on the Ag layer.

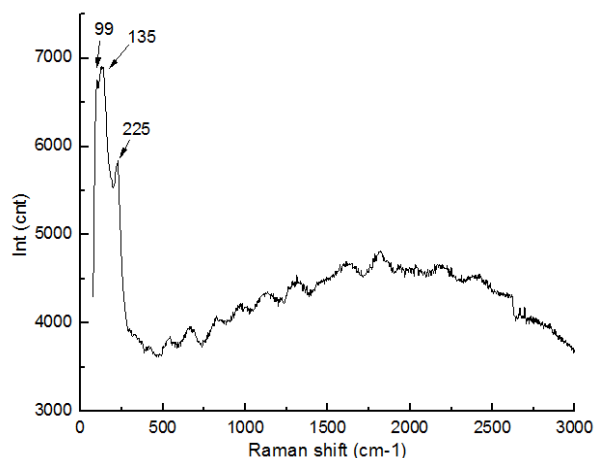


Figure 7. The Raman spectrum of the Ag/AgCl layer.

3.2. Characterization of the Fabricated Ag/AgCl/Agarose Electrode

The thickness of the Ag/AgCl/agarose electrodes measured by Dektak 6M was $28.6 \mu\text{m} \pm 3.5 \mu\text{m}$. The thickness of the agarose layer could be varied by adjusting to the concentration of the agarose solution.

On the other hand, the physical stability of the modified electrodes was good. After immersed in DI water and pH 7 solution for 2 hours, the fabricated electrodes remained stable. The surface of the electrodes was not damaged and the Ag/AgCl/agarose layer was still on the electrodes. Fig. 8 shows the electrodes before and after immersed in DI water, pH7 solution for 2 hours.

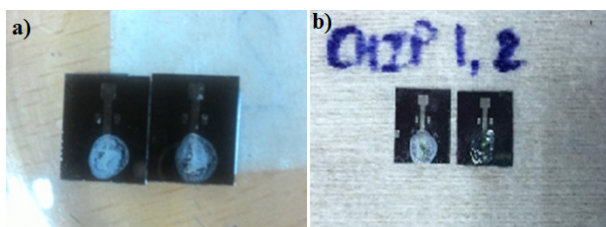


Figure 8. The photos of the Ag/AgCl/agarose electrodes before (left) and after (right) immersed into DI water and pH7 solution for 2 hours.

The right hand side electrode (Fig. 8b) was just taken out of the solution after 2 hours of immersing, then the electrode was left at room temperature for 10-15 minutes to dry out. After drying, the electrode came back as the left hand side electrode of Fig. 8b. It was clearly shown that the modified electrode remained unchanged after 2 hours of

immersing in DI water and pH7 solution.

3.3. Electrochemical Characterization

Electrochemical characterization of the fabricated Ag/AgCl electrodes was performed by comparison of the potential difference between the fabricated Ag/AgCl electrodes with the commercial Ag/AgCl reference electrode. Both the Ag/AgCl electrodes were immersed in a pH 7 buffer and the OCP measurement was performed by the Autolab PGSTAT 302N, Metrohm, the Netherlands. The OCP mean value of the Ag/AgCl electrodes after 5 repeated measurements was $20.3 \pm 2.7 \text{ mV}$. The potential difference is lower and more stable in comparison with the reported potential variations (187 mV in [9, 28] and $27 \pm 3 \text{ mV}$ in [9, 28]). The difference in dimension of the electrodes is attributed to the difference in the OCP values between the fabricated Ag/AgCl electrode and the commercial Ag/AgCl reference electrode. The measurements had good repeatability with acceptable errors. However, it was observed that after the OCP measurements, the Ag/AgCl electrode layer on the chip was slightly damaged (as shown in Fig. 9) and the Ag/AgCl layer was fully degraded after 4 times of OCP measurements.

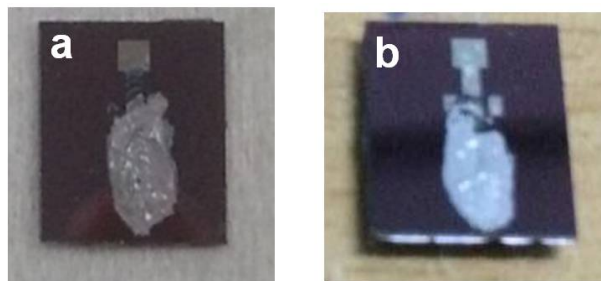


Figure 9. The photos of the Ag/AgCl electrode before (a) and after OCP measurements (b).

The electrochemical properties of the Ag/AgCl/agarose electrodes were determined by using the same experimental set up as with the Ag/AgCl electrodes. In the first week of measurements, the OCP mean value of the Ag/AgCl/agarose electrodes (after 5 repeated times) was 252 mV and the deviation values of five (5) times of measurement was $\pm 14 \text{ mV}$. One week later, the Ag/AgCl/agarose electrodes were measured again. The OCP mean value of the modified electrodes after 3 repeated times was $187 \pm 17 \text{ mV}$. The large change of the OCP values (approximately 9 to 10 times) of the Ag/AgCl/agarose electrodes was attributed to the change of the structure of the modified electrodes. However, it was found that the addition of the agarose layer on the Ag/AgCl electrodes helped to enhance durability of the Ag/AgCl electrodes (8 times of measurements).

The potential difference between the fabricated Ag/AgCl, Ag/AgCl/agarose electrodes and the commercial Ag/AgCl electrode was the result of directly contact between the fabricated Ag/AgCl, Ag/AgCl/agarose

electrode and the electrolyte solution without a protection layer. Without the protection layer which was filled with high concentration of Cl^- , the electrode-electrolyte contact of the fabricated Ag/AgCl electrode caused the activity of Cl^- unstable. This instability could also make the difference in OCP value of the fabricated Ag/AgCl electrode and the commercial Ag/AgCl electrode. This potential variation could be reduced by coating a protection layer which was full-filled with Cl^- on the Ag/AgCl electrode layer as suggested in the ref. [4, 9].

3.4. Optimal Condition Demand

The Ag/AgCl reference electrodes with specific design were fabricated by photo-lithography, physical and chemical deposition in a very simple process. The potential difference between the fabricated electrode and the commercial Ag/AgCl electrode was 20.3 ± 2.7 mV, which is lower and more stable than others publish reports [9, 28]. The agarose layer acted as a protection layer in order to enhance the durability of the fabricated electrode. The potential difference increase could be due to the increase in thickness of the electrodes. The durability of the fabricated electrode could be improved by storing the electrode in the solution which has high concentration of Cl^- . The potential variation can be reduced by decreasing the thickness of the electrode (decrease the thickness of the AgCl layer or the agarose layer).

4. Conclusions

The Ag/AgCl reference electrodes with a thickness of 5 μm and high purity were fabricated by lithography, sputtering deposition technique and chemical deposition from reversibility of the $\text{Ag}(\text{NH}_3)_2\text{Cl}$ complex in a simple process. The fabricated Ag/AgCl electrodes and the Ag/AgCl/agarose electrodes were still stable after undergoing the electrochemical measurements. The potential difference of the fabricated electrodes was lower and more stable in comparison with the reported potential variations with an acceptable error. Addition of the agarose layer as the protection layer of the Ag/AgCl electrodes enhanced the durability of the modified electrodes. The potential variation could be reduced by coating a protection layer which was filled with a high concentration of Cl^- . The results show that the fabricated Ag/AgCl electrode could be used as a planar reference electrode in potentiometric sensors for aquacultural farming.

Acknowledgements

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