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Investigation of a Thin-Film Quasi-Reference Electrode Fabricated by Combined Sputtering-Evaporation Approach

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Abstract
This paper presents the development of a thin-film quasi-reference electrode (tQRE), which was fabricated by sputtering silver (Ag) on a conducting gold layer. The Ag layer was subsequently covered by silver chloride (AgCl) with the aid of e-beam evaporation. The functionality of the tQREs as reliable reference electrodes was confirmed by observing the potential response in solutions with various chloride ion concentrations. The influence of solution pH on the potential change of the tQREs was evaluated. In the solution with controlled ionic strength, the tQREs were able to provide stable and consistent potential outputs. Experimental investigation of the electrochemical sensors with integrated tQREs demonstrated potential applicability of the tQREs to be incorporated into miniaturized and disposable lab-on-a-chip sensors for point-of-care/in-situ measurements.

Keywords: Cyclic voltammetry; Electrochemistry; Microfabrication; Quasi-reference electrode; Silver/silver chloride

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1. Introduction

The need to perform point-of-care monitoring and diagnosis has driven the rapid development of miniaturized, portable, and disposable lab-on-a-chip (LOC) electrochemical sensors. A variety of chemical and biological molecules, such as dissolved oxygen [1-3], toxic metal ions [4-6], dopamine [7-9], pathogens [10-11], viruses [12-13], etc. can be directly detected without complicated operation and intricate analysis. In general, an electrochemical sensor consists of a working electrode, a counter/auxiliary electrode, and a reference electrode. The interaction between the analyte of interest and the sensing element present on the working electrode will result in either a flow of charge or a change of potential to be measured. During the measurement, the reference electrode plays a significant role since it provides a reference point to the working electrode. Hence, a stable reference electrode is critical for electrochemical sensors to generate reliable and accurate outputs.

Among all types of reference electrodes, conventional silver/silver chloride (Ag/AgCl) reference electrode has gained more attention due to the simple construction and inexpensive manufacturing. Briefly, a high-purity Ag wire is chloridized to have a coating layer of AgCl, which is immersed in a glass tube filled with 3 M, 3.5 M, or saturated sodium chloride (NaCl) or potassium chloride (KCl) electrolyte. The redox reaction governing the Ag/AgCl reference electrode inherently has a high exchange current density [14], making the potential insusceptible to random charge movement across the electrode-electrolyte interface. However, the bulky size of conventional Ag/AgCl reference electrode limits its application for point-of-care measurements. In addition, the leakage of internal filling electrolyte to the test solution may cause prominent change of the chloride ion (Cl$^-$) activity, which will significantly alter the potential of the liquid junction as well as that of the reference electrode. Therefore, the development of Ag/AgCl quasi-reference electrodes (QREs), which completely excludes the aqueous filling electrolyte, has been of great interest to academic researchers.

Although the potential of QREs is exceptionally affected by the condition of test solution owing to the lack of thermodynamic equilibrium, there are still many valuable advantages of QREs, e.g. elimination of liquid junction potential, reduced ohmic resistance, simplicity of electrode design, and prevention of electrolyte contamination. A lot of researchers have reported satisfactory performance employing Ag/AgCl QREs for various applications. Branch et al. [15] developed an optically transparent thin-film electrode chip for fluorescence spectroelectrochemical determination, in which the Ag/AgCl QRE was fabricated by first electroplating an Ag layer on top of a platinum (Pt) electrode. The AgCl layer was then chemically formed by covering the Ag surface in the solution of $FeCl_3$. Ragones et al. [16] reported a biocompatible electrochemical chip to detect the biomarker alkaline phosphatase in a cell culture plate, in which the Ag/AgCl QRE was also prepared by a double-step process. It involved a step of Ag electroplating in the solution of $AgNO_3$ and another step of anodization in the solution of HCl to form an AgCl layer. Musa et al. [17] designed a potentiometric system with ion-selective electrode array to monitor the solution pH, in which the Ag/AgCl QRE was made by screen-printing the Ag/AgCl ink on graphite track. The ink was then cured by heating both Ag/AgCl and graphite layers at 120°C for 20 min. To circumvent the aforementioned cumbersome fabrication procedures, a thin-film quasi-reference electrode (tQRE) manufactured by a simple approach of combined sputtering and evaporation is proposed in this work. The tQREs are constructed on a type of liquid crystal polymer (LCP) substrate, which renders the electrodes favorable flexibility due to the unique material properties of the LCP. The performance of the tQREs is comprehensively evaluated when they are subjected to different test conditions. Experimental investigation reveals that the tQREs are competent as solid-state reference electrodes, leading to a possible integration on LOC electrochemical sensors for point-of-care/in-situ applications.

2. Experimental

2.1. Fabrication of Thin-Film Quasi-Reference Electrode

To fabricate the tQREs, a LCP substrate (ULTRALAM 3850, 100 µm thickness) purchased from Rogers Corporation, USA was attached to a 4-inch silicon wafer. The protective metal layer covered on the substrate was initially removed by chemical etching, after which the substrate was thoroughly cleaned with acetone to remove impurities. Subsequently, standard photolithography was performed to make the pattern of the reference electrode, connecting lead and contact pad (as shown in Figures 1A and 1B). The dimensions are 4 mm × 0.8 mm, 1.5 mm × 0.1 mm, and 1.5 mm × 1.5 mm, respectively. Thereafter, a chromium/gold (Cr/Au: 50/300 nm) layer was deposited to form a conducting layer for the tQREs. Employing the same pattern, the Ag (200 nm) layer was deposited using a magnetron sputtering system. Finally, a layer of AgCl (300 nm) was directly formed on the Ag layer using an electron-beam evaporator. The thickness of each layer was carefully controlled during fabrication and measured by a surface profilometer to ensure the consistency of the fabrication. Figure 1C shows the photograph of a tQRE after dicing from a batch of fabrication.

Fig. 1. Schematic drawing of (A) top-view and (B) cross-section to show the structure of the tQRE. (C) Photograph to show a tQRE after fabrication.

The flexibility of the tQREs is verified by continuously bending the tQREs ten times with a tweezer, as shown in Figure 2A. After each time of bending, the resistance value of each tQRE was measured. The obtained results are presented in Figure 2B, in which the resistance values remain constant through ten times of consecutive bending. The relative standard deviation (RSD) of the resistance change is calculated as only 0.36%, demonstrating that the functionality of the tQREs can be well maintained after a few times of physical bending. Prior to experiments, one side of each tQRE was trimmed to keep one connecting lead and one contact pad. The tQREs were packaged using conductive epoxy to link a wire with the contact pad. Thereafter, non-conductive epoxy was applied to cover both connecting lead and contact pad for proper sealing as well as electrical insulation.

Fig. 2. (A) Photograph to show physical bending of the tQRE using a tweezer. (B) Resistance change of the tQREs through ten times of consecutive bending.

To explore potential integration of the tQREs on LOC devices, a batch of electrochemical sensors were fabricated by integrating the proposed tQRE with one Au working electrode and one Au counter electrode on a single piece of LCP substrate, as depicted in Figure 3. The sensors were packaged by wiring one set of the contact pads of three electrodes using conductive epoxy. The other set of the contact pads together with all connecting leads were insulated using non-conductive epoxy.

Fig. 3. Photograph of the electrochemical sensor fabricated by integrating tQRE with Au working and counter electrodes on a single piece of LCP substrate.

2.2. Chemicals and Apparatus

All chemicals and reagents used in this study were of analytical grade. Throughout the experiments, ultrapure water (18.2 MΩ·cm) collected from a Milli-Q system (Merck, Singapore) was used to prepare the solutions. Potassium hexacyanoferrate (Ⅲ) ($K_3[Fe(CN)_6]$) powder and KCl powder were purchased from Sigma-Aldrich, Singapore. Buffer solutions having pH values of 5, 6, 7, 8, and 9 were obtained from Merck, Singapore and used without further treatment. Bismuth (Bi) nanoparticles powder (99.9%) was purchased from US Research Nanomaterials, USA. Standard lead (Pb) stock solution (1000 mg/L) was supplied by Merck, Singapore. Acetate buffer (pH 4.6) purchased from Sigma-Aldrich, Singapore was used as supporting electrolyte for the Pb test solutions. Commercial Ag/AgCl reference electrode with 3 M NaCl internal electrolyte, Au working electrode (3 mm diameter), and Pt counter electrode (0.5 mm diameter, 50 mm length) were purchased from Alpha Analytical, Singapore. All measurements were recorded using a CHI 600C electrochemical workstation (CH Instruments, USA).

2.3. Electrochemical Experiments

The first experiment was to evaluate the response of the fabricated tQREs in solutions containing various Cl^- concentrations. The potentials were measured for 5 min with respect to the commercial Ag/AgCl reference electrode. Thereafter, the response of the tQREs in solutions having different pH values was evaluated. Similarly, the potentials were recorded for 5 min. To test the stability of the tQREs, the potentials were continuously monitored for 10 hrs in buffer solution (pH 7) with 200 mM KCl. The possibility of utilizing tQREs for electrochemical analysis was assessed by conducting a series of cyclic voltammetry (CV) experiments together with commercial Au working electrode and Pt counter electrode. The solutions used for CV testing were prepared by dissolving proper amount of powder into ultrapure water to obtain a final concentration of 2 mM $K_3[Fe(CN)_6]$ and 200 mM KCl. The voltammograms were recorded with an initial and final potential of 0.6 V, a switching potential of -0.2 V, and varied scan rates. Finally, the electrochemical sensors with integrated tQREs were tested by performing square wave anodic stripping voltammetry (SWASV) experiments. A deposition potential of -0.9 V was initially applied for 90 s under quiescent condition. The voltammograms were then recorded in a potential range from -0.65 to -0.3 V with a step potential of 5 mV, amplitude of 25 mV, and a frequency of 50 Hz. All experiments were carried out at room temperature. Data are presented as the mean values and sample-to-sample standard deviations obtained from the measurements using three devices.

3. Results and Discussion

3.1. Surface Characterization of Thin-Film Quasi-Reference Electrode

The surface morphology of the tQREs after fabrication was observed using a scanning electron microscope (SEM). As shown in Figure 4A, the evaporated AgCl aggregates together to form a number of particles, which are evenly distributed on the Ag layer. Some of the particles are closely packed into larger patches, which can be seen in the lower section of Figure 4A. The elemental composition of the tQREs' surface was further examined with the aid of energy-dispersive X-ray spectroscopy (EDS). The analysis was conducted with an inspection area of about 1,000 μm^2. One representative EDS spectrum obtained is shown in Figure 4B and the average weight and atomic percentage data are summarized in the inset. The EDS result confirms the successful fabrication of sputtered Ag together with evaporated AgCl on the Au conducting layer of the tQREs.

Fig. 4. (A) SEM image to show the surface morphology of the tQREs. (B) One representative EDS spectrum obtained by analyzing the surface of the tQREs.

3.2. Potential Response in Solutions with Various Cl^- Concentrations

To investigate the effect of Cl^- concentration on the potential variation of the tQREs, buffer solutions (pH 7) containing 10, 50, 100, 200, 400, and 1000 mM KCl were prepared. The potential response of the tQREs was observed in each solution (Figure S1 in the supplementary material). The results are plotted in Figure 5, where the potential keeps reducing when the Cl^- concentration is increased. An inverse linear relationship is obtained between the potential and the logarithm of Cl$^-$ concentration. Such trend is in line with the prediction from Nernst equation, in which the electrode potential of Ag/AgCl reference electrode can be expressed as [18]:

$$E = E^0 - \frac{RT}{nF} ln\left(\frac{\gamma_{cl^-}}{C^0} C_{cl^-}\right) \qquad (1)$$

where E, electrode potential (V); E^0, standard electrode potential (V); R, universal gas constant (8.31 J/(K•mol)); T, absolute temperature (K); n, number of electrons transferred in the redox reaction ($n = 1$ for Ag/AgCl reference electrode); F, Faraday constant (96,485.34 C/mol); γ_{cl^-}, activity coefficient of chloride ion; C_{cl^-}, concentration of chloride ion in solution (mol/L); C^0, standard concentration (1 mol/L). Equation (1) can be rewritten as:

$$\begin{aligned} E &= E^0 - \frac{2.3RT}{nF} \log\left(\frac{\gamma_{cl^-}}{C^0} C_{cl^-}\right) \\ &= E^0 - \frac{2.3RT}{nF} \log\left(\frac{\gamma_{cl^-}}{C^0}\right) \\ &\quad - \frac{2.3RT}{nF} \log(C_{cl^-}) \qquad (2) \\ &= a - b \log(C_{cl^-}) \end{aligned}$$

where $a = E^0 - 0.0002T \log(\gamma_{cl^-})$ and $b = 0.0002T$ are two constants at fixed temperature. From equation (2), it can be derived that the electrode potential is inversely related to the logarithm of Cl$^-$ concentration.

This result demonstrates that the fabricated tQREs can function as accurate and operational reference electrodes as long as the ionic strength of the solution is maintained. A similar observation was reported by Matsumoto et al. [19], in which micro-planar Ag/AgCl QRE was coated by an adhesion layer of γ-aminopropyltriethoxysilane and a diffusion layer of perfluorocarbon polymer. The micro-planar QREs developed by Matsumoto et al. showed Nernst response in the Cl$^-$ concentration range from 50 to 536 mM with an average slope value of −57.7 ± 1.27 mV per decade. When the Cl$^-$ concentration is below 50 mM, the behavior of the micro-planar QREs deviates from Nernst response, which is evident by a significant amount of negative potential shift (Figure 4 in [19]). The tQREs proposed in this work were able to exhibit Nernst response in a wider Cl$^-$ concentration range from 10 to 1000 mM compared to the micro-planar QREs. The average slope value of the tQREs is calculated as −65.5 ± 2.23 mV per decade, which is slightly higher than that of the micro-planar QREs. The difference of electrochemical performance between the micro-planar QREs and the proposed tQREs could be due to the distinct morphology of the electrode surface.

Fig. 5. Effect of Cl$^-$ concentration on the potential change of the tQREs recorded with respect to commercial Ag/AgCl reference electrode.

3.3. Potential Response in Solutions with Various pH Values

The influence of solution pH on the potential change of the tQREs was further investigated. To control the ionic strength, 200 mM KCl was added to each solution. The potentials of the tQREs were measured with respect to commercial Ag/AgCl reference electrode for 5 min (Figure S2 in the supplementary material). The results obtained are shown in Figure 6, in which the potential variation is about 5 mV when the solution is acidic (from pH 5 to 7). On the other hand, the potential drifts around 10 mV when the solution is alkaline (from pH 7 to 9). Such potential fluctuation is probably caused by the mixed potential formed between the Ag/AgCl layer and the conducting layer of the tQREs. In the course of testing, the side surface of the conducting layer is also exposed to the solution. Therefore, it is possible that the mixed potential slightly varies when the acidity/alkalinity of the solution is altered. Suzuki et al. [20] observed a similar trend for their proposed Ag/AgCl reference electrode, which was covered by a polyimide layer. They detected a potential drift of about 12 mV within a pH range from 4.03 to 10.03 [20]. One possible solution to reduce the potential drift for the tQREs is to establish an insulation film to shield the peripheral surface of the conducting layer. This could be achieved by introducing another deposition step when the tQREs are fabricated or applying some polymer materials when the tQREs are packaged. Such insulation film may also improve the operational durability of the tQREs.

Fig. 6. Effect of solution pH on the potential change of the tQREs recorded with respect to commercial Ag/AgCl reference electrode.

3.4. Stability of Thin-Film Quasi-Reference Electrode

The stability of the tQREs was studied by continuously recording the potential response for 10 hrs in the solution (pH 7) of 200 mM KCl. The output is illustrated in Figure 7, in which no significant change of potential is observed. The total potential drift is only about 4.57 mV within the entire measurement time. This signifies that the tQREs are capable of maintaining proper functionality for a long period of time if the test environment does not change dramatically. This is the common scenario for LOC sensors, where a small amount of analyte solution is introduced to the sensing component of the devices [21-25]. Therefore, it is possible to incorporate the proposed tQREs into compact LOC electrochemical sensors, considering the simplicity of its structure and the compatibility of its production with other microelectromechanical systems (MEMS) fabrication processes [26-27].

Fig. 7. Potential change of the tQRE recorded for 10 hrs with respect to commercial Ag/AgCl reference electrode in the solution (pH 7) of 200 mM KCl.

3.5. Applicability of Thin-Film Quasi-Reference Electrode

To explore the applicability of the tQREs, a series of CV experiments were carried out in the solution (pH 7) of 2 mM $K_3[Fe(CN)_6]$ and 200 mM KCl. The scan rates were chosen as 30, 50, 100, 150, 200, and 250 mV/s (Figure S3 in the supplementary material). The reduction potentials measured with respect to the tQREs are shown in Figure 8A. It can be found that all potentials are quite consistent among eighteen times of consecutive measurements. The RSD of the potential change is as low as 1.30%, which implies a high output reproducibility of the tQREs.

As the CV experiments were conducted under quiescent condition, the peak current should be linearly correlated with the square root of the scan rate, according to the Randles–Sevcik equation [28]:

$$i_p = 0.4463\frac{n^{3/2}F^{3/2}}{R^{1/2}T^{1/2}}D^{1/2}v^{1/2}AC \qquad (3)$$

where i_p, peak current (A); D, diffusion coefficient of the electroactive species (cm^2/s); v, scan rate (V/s); A, electrode area (cm^2); C, bulk concentration of the electroactive species (mol/cm^3). As depicted in Figure 8B, the reduction peak currents quantified from CV voltammograms are plotted against the scan rates. Herein, a linear fitting straight line with a coefficient of determination (R^2) value of 0.999 is obtained between the magnitude of peak current and the square root of scan rate, which completely matches with equation (3). This result indicates that the tQREs are able to provide a stable reference potential to the working electrode, thereby allowing accurate output to be produced over multiple measurements.

Fig. 8. (A) Reduction potentials recorded with respect to the tQREs in eighteen consecutive CV experiments. (B) Fitting line between the magnitude of the reduction peak current and the square root of the scan rate.

To demonstrate potential application of the tQREs in the development of LOC devices, the electrochemical sensors with integrated tQREs were used to detect Pb metal ions in solutions. The working electrode of each sensor was modified by drop-casting 6 µL solution containing 100 mg/L Bi nanoparticles. The sensors were initially immersed in the solution of 0.1 M acetate buffer. Subsequently, the Pb^{2+} concentration was elevated from 10 to 110 µg/L with an increment of 20 µg/L. The SWASV voltammograms recorded are shown in Figure 9, in which legible stripping peaks can be clearly distinguished near the potential of -0.45 V. In addition, the magnitude of the stripping peak is gradually enlarged, which corresponds to the increase of Pb^{2+} concentration in the test solutions. More importantly, all stripping peak potentials (around -0.45 V) are well aligned as presented in the voltammograms, indicating stable performance of the tQREs throughout the whole process of the measurements.

Fig. 9. One representative series of square wave anodic stripping voltammograms recorded for the electrochemical sensors with integrated tQREs.

4. Conclusions

In this study, a thin-film QRE fabricated by evaporating AgCl on a pre-sputtered Ag layer is proposed. The AgCl material shapes into densely-packed patches that are uniformly spread on the electrode surface. By virtue of electrochemical assessment, it is unambiguous that the tQREs display Nernst response and the electrode potential is less sensitive to the change of solution pH. Application of the tQREs in electrochemical sensors demonstrates favorable capability to consistently produce stable and reproducible reference potentials. The simplicity and compatibility of the electrode construction render a great potential for the tQREs to be integrated on miniaturized and disposable LOC devices for point-of-care/in-situ applications.

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