Comparative Study of Planar Ag/AgCl Quasi-Reference Electrodes Developed on PCB

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***Abstract*—This paper presents a comparative study of different fabrication methods for planar Ag/AgCl quasi-reference electrodes (RE) on a printed circuit board (PCB) aimed at integration into portable electrochemical biosensors. Three fabrication techniques based on electroplating and screen printing are studied, along with two chlorination methods to convert the electroplated silver layers into silver chloride layers. The comprehensive characterisation of the three REs demonstrates the stability of the electrodes compared to those of commercially available planar reference electrodes. A drift rate as low as 2.2 mV/day is observed over 7 days for electrodes developed through Ag electroplating and chlorination with NaOCl, making these REs suitable for continuous biosensing applications.**

***Index Terms*—electrochemical biosensors, Ag/AgCl quasi-reference electrode, PCB, electrodeposition**

I. Introduction

Electrochemical biosensors have emerged as powerful tools for the rapid, sensitive, and cost-effective detection of biomarkers in medical diagnostics, environmental monitoring, and food safety applications [1]. A critical component of these biosensing platforms is the reference electrode, which provides a stable potential. There is increasing interest in miniaturised planar reference electrodes that can be integrated into portable and disposable biosensor devices [2].

Printed circuit board (PCB) technology offers a low-cost and scalable platform for the development of miniaturised electrochemical biosensors that seamlessly integrate electrodes, microfluidics, and electronics [3]. Recent advances in materials and fabrication techniques have enabled the development of planar Ag/AgCl reference electrodes on PCBs. However, despite their potential, Ag/AgCl reference electrodes developed on PCB substrates face challenges such as silver oxidation, chloride depletion, and potential drift [4].

Existing fabrication techniques include direct screen printing of Ag/AgCl [5], or a two-step process with sputtering [6] or electrodeposition [7] of Ag, followed by its chlorination to create an Ag/AgCl layer. Two main chlorination methods have been used that involve the treatment of the Ag layer with sodium hypochlorite (NaOCl) [3], [8] or ferric chloride ($FeCl_3$) [9], [10]. The optimal chlorination method remains uncertain, as NaOCl and ($FeCl_3$) treatments differ in their reaction kinetics and AgCl layer properties.

Additional materials, such as polymer coatings [5], [11] or salt matrix modifications [12], can be applied to the surface of the electrode to enhance stability and extend its useful life However, incorporating these layers increases fabrication complexity and cost, potentially limiting their practicality for low-cost applications. Moreover, the deposition of such layers often requires specialised substrates or surface modifications [13], [14] to ensure proper adhesion and functionality, further complicating the manufacturing process.

This study compares three fabrication methods for developing planar reference electrodes (RE) on PCB substrates: (i) screen printing of Ag/AgCl, (ii) Ag electroplating followed by chlorination with sodium hypochlorite, and (iii) Ag electroplating followed by chlorination with ferric chloride. We present a comprehensive analysis of the resulting electrode surfaces and their electrochemical performance to develop a simple, stable, and cost-effective planar RE suitable for continuous electrochemical monitoring in portable biosensing devices.

II. Materials and Methods

A. Materials

Silver electroplating solution (NB Semiplate Ag 100) and Gold electroplating solution (NB Semiplate Au 100) from NB Technologies were used. Sodium hypochlorite solution (6-14% active chlorine) from Sigma-Aldrich and iron (III) chloride ($FeCl_3$) from Merck were used. Ag / AgCl paste (60Ag/40AgCl) was purchased from Sigma-Aldrich. Acetone (HPLC grade) and isopropyl alcohol (HPLC grade) were purchased from Sigma-Aldrich.

B. Electrodes

PCBs with circular electrodes of 5 mm diameter were fabricated at JLCPCB with an ENIG (Electroless Nickel Immersion Gold) surface finish. A 1 mm protective overlayer was also deposited on the PCB surface to cover the electrode edges to fully seal the underlying nickel and copper layers. The exposed nickel would otherwise interfere with electrochemical measurements [15], [16].

A commercially available (non-planar) silver/silver chloride glass reference electrode (BASI MF-2056) was used as the reference electrode in open circuit potential and cyclic voltammetry measurements. A platinum mesh electrode (size 4 cm^2,

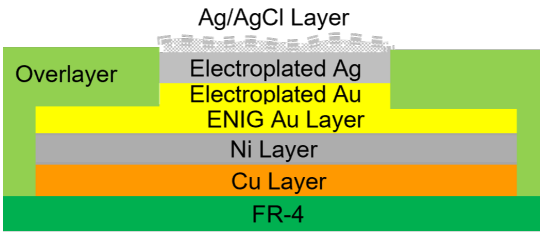

Fig. 1. Illustration of electrode stack in the developed planar RE with Ag/AgCl on PCB

0.1 mm wire diameter from Sigma-Aldrich) was used as a counter electrode in cyclic voltammetry measurements.

A planar Quasi RE on a commercially available screen-printed electrode (Metrohm DRP C-110) was used as a benchmark in drift analysis.

C. Equipment

All experiments were performed with an AutoLab PGSTAT 204 at room temperature. Scanning electron microscopy (SEM, using a JEOL JSM IT-100 machine) was used for topographical imaging. Atomic force microscopy (AFM, Bruker ICON) was used for high-resolution surface characterisation. Furthermore, Energy-Dispersive X-ray (EDX, with JEOL JSM IT-100) Spectroscopy was performed to examine the elemental composition.

III. Development of RE on PCB

A. Au Electroplating

It was observed that the ENIG gold on the PCB electrodes was not suitable for silver plating due to the existence of pinholes, surface defects, and potential contaminants. Therefore, an extra step was introduced where a layer of Au was electroplated on top of the ENIG Au layer, as explained here.

The PCBs were first cleaned by sonication in acetone for 10 minutes, followed by sonication in IPA for 10 minutes, and then thoroughly rinsed with deionised water.

The gold electroplating was performed using a pulsed galvanostatic deposition (PGD) technique in the presence of the gold electroplating solution. The PGD method was chosen to achieve a smoother and more uniform surface compared to that obtained by direct current (DC) deposition. PGD also allows better control over nucleation and growth processes, reducing stress and improving adhesion [17], [18]. An average current density of 1.5 mA/cm^2, a pulse frequency of 100 Hz, and a duty cycle of 50% were used in PGD.

SEM and AFM imaging confirm that the grains on the ENIG Au surface are completely coated with Au after Au electroplating, and the electrode surface has become smoother (see Figure 2). The surface roughness of the electrode also decreased from 280 nm rms to 50 nm rms after Au plating.

B. Ag Electroplating

Silver electrodeposition was then performed using an Ag electroplating solution with an alkaline cyanide-free formulation. A PGD method was employed here as well. An average current density of 30 mA/cm^2 was applied over a deposition time of 200 seconds. The frequency and duty cycle were set to 100 Hz and 50%, respectively.

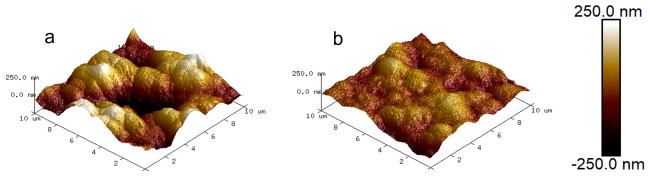

Fig. 2. AFM images of (a) ENIG and (b) gold electroplated PCB

C. Ag Chlorination

Two chlorination methods were used. In the first method, the Ag-plated PCB electrodes were immersed in NaOCl for 600 seconds. The deposition time was selected following previously published works [3].

In the second method, Ag-plated PCB electrodes were immersed in $FeCl_3$ for 60 seconds, following a similar technique in [9].

The complete electrode stack is illustrated in Fig. 1. The surface properties were methodically evaluated at each step of fabrication. Figure 3 presents SEM images that show progressive changes at every stage of the fabrication process.

D. Ag/AgCl Screen Printing

A homogeneous, thin Ag / AgCl paste layer was manually deposited on Au-plated electrodes. The electrodes were then left to dry at ambient temperature for 24 hours. A summary of the three fabrication methods is given in Table I.

IV. Results and Discussion

A. RE Stability

The stability of freshly prepared PCB REs was evaluated by measuring the OCP (Open Circuit Potential) between the individual electrode and a commercially available glass Ag/AgCl electrode over 24 hours. Electrodes were dipped in a pH buffer solution (pH 4, 7 or 9) or 3M KCl. The results are presented in Fig. 4. The drift values observed for QRE-Na are smaller than those of the commercial screen-printed reference electrode (Com-SPRE), indicating that QRE-Na is a viable alternative to commercial screen-printed reference electrodes.

The elemental composition of the reference electrodes before and after the stability test (24-hr OCP measurement in pH 7) is listed in Table II. Notably, the total loss of chlorine in QRE-Fe and SP-RE electrodes indicates a lack of stability of the electrode surface. The percentage of chlorine in QRE-Na decreases from 15% to 6%, indicating only a partial chloride loss. These results reveal QRE-Na as the best-performing out of the three electrodes developed in this work. We therefore carried out a more extensive characterisation of QRE-Na as detailed in the next subsections.

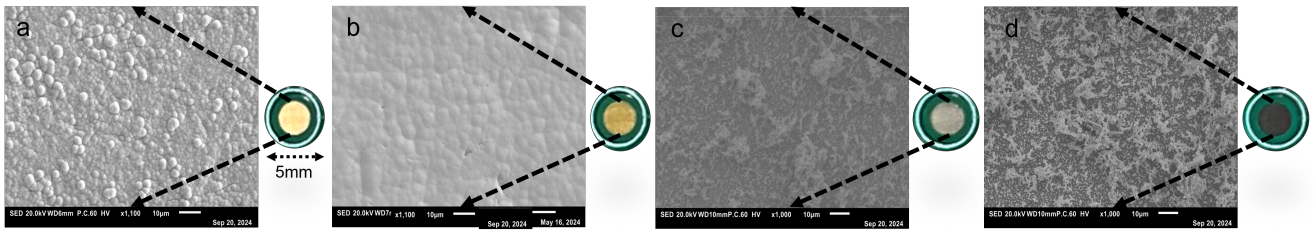

Fig. 3. Optical and SEM images obtained after each fabrication step. (a) ENIG electrodes, (b) after Au-electroplating, (c) after Ag-electroplating, and (d) after chlorination with NaOCl.

TABLE I
SUMMARY OF THE THREE FABRICATION METHODS FOR RE ON PCB

Quasi Reference Electrode ID	Method	Electrode Stack	AgCl Development Technique
SP-RE	Screen Printing	ENIG/Au/Silver Paste	-
QRE-Fe	Au/Ag Electrodeposition	ENIG/Au/Ag	FeCl Chlorination
QRE-Na	Au/Ag Electrodeposition	ENIG/Au/Ag	NaOCl Chlorination

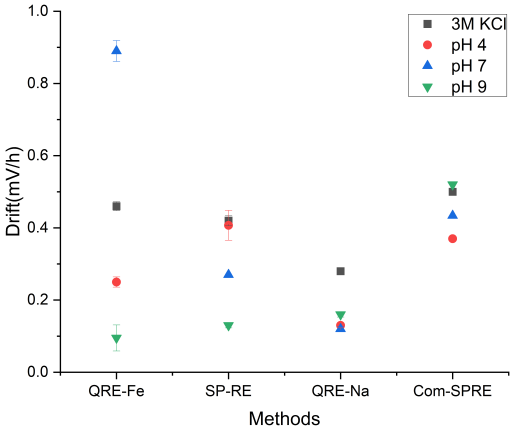

Fig. 4. Comparison of the drift performance of different reference electrode types (QRE-Fe, SP-RE, QRE-Na, Com-SPRE) in pH buffer solutions and 3M KCl. Drift was measured over 20 hours after a 4-hour stabilisation period, with electrodes stored in the solutions for 24 hours. Error bars show the standard deviation from three electrodes.

B. Long-term Stability of QRE-Na

The OCP measurement was extended to 7 days to understand how extended exposure to a solution (of pH 7) affects the stability of the QRE-Na electrodes. The results are shown in Figure 5. The average drift rate is measured to be 2.2 mV/day.

TABLE II
EDX ANALYSIS OF THE QREs BEFORE AND AFTER STABILITY TEST (IN PH 7 FOR 24 HOURS) (ATOMIC %)

Elements	QRE-Na		QRE−Fe		SP-RE	
	Before	After	Before	After	Before	After
Ag	84.66	93.82	86.69	84.23	83.22	93.98
Cl	15.34	6.18	13.31	0	16.79	0
Au	0	0	0	13.17	0	3.16
Cu	0	0	0	1.73	0	1.98
Ni	0	0	0	0.87	0	0.88

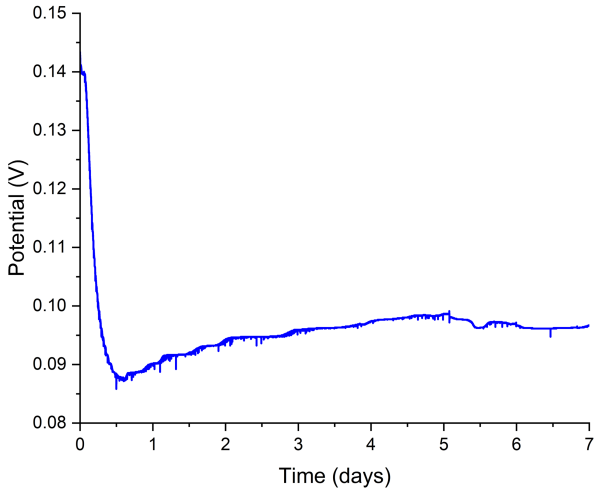

Fig. 5. The voltage between the QRE-NA and a commercial Ag/AgCl electrode (non-planar) measured over 7 days. The average drift rate is 2.2 mV/day from t = 4 hours to the end of day 7.

This is comparable to the drift rates reported for commercially available non-planar Ag/AgCl reference electrodes (1 mV/day [19]). Table III shows a table comparing the performance of QRE-NA with similar structures of PCB-based QREs.

TABLE III
COMPARISON WITH STATE-OF-THE-ART PLANAR RE ON PCB ELECTRODE STACKS AND POTENTIAL DRIFT

Ref.	Electrode Stack	Chlorination	Drift (mV/day)
[3]	Cu/Ag/AgCl/PDMS	NaOCl	1
[13]	Cu/Ag/AgCl/Agar/PVC/Membrane	KCl/HCl	24
[14]	Cu/Ag/AgCl/PVC/Ionic Liquid	KCl/$AgNO_3$	10.8
This work	ENIG/Au/Ag/AgCl	NaOCl	2.2

The observed drift in the OCP measured during the 7 day period may be attributed to the chloride depletion from the Ag/AgCl electrode as previously shown by other researchers [19], [20], as well as the oxidation of Ag, which is also shown to cause drift in other works [2], [21].

C. Functionality test

Repeated cyclic voltammetry (CV) measurement was performed to assess variations in the electrochemical performance of the QRE-Na electrodes and investigate their electron transfer properties. CV was carried out with a scan rate of 0.05 V/s in a solution containing 0.1 M KCl, 0.1 mM ferricyanide

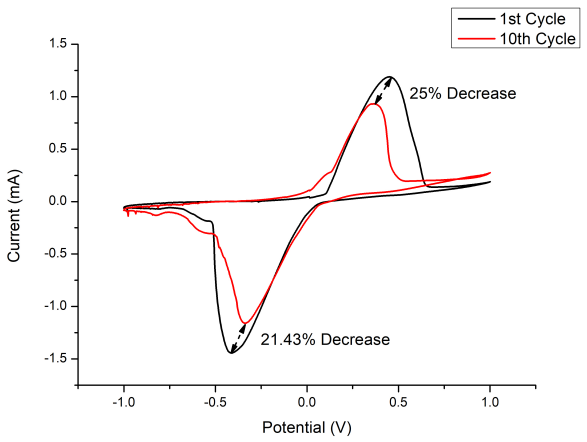

Fig. 6. Cyclic voltammograms (in 0.1 M KCl, 0.1 mM ferricyanide and 1 mM potassium ferrocyanide) using the QRE-Na as working electrode, a non-planar Ag/AgCl reference electrode and a platinum mesh counter electrode.

and 1 mM potassium ferrocyanide. Figure 6 shows the first and tenth voltammograms.

A deviation in the peak positions was observed: the anodic peak shifted by 91 mV, and the cathodic peak shifted by 76 mV. These shifts suggest changes in the electrode's electrochemical properties over multiple cycles. The observed difference can be primarily attributed to the elevated chloride concentration in the solution. This high chloride content leads to an abundance of chloride species surrounding the electrode surface, which in turn promotes an equilibrium between the dissolved chloride in the solution and the silver chloride deposited on the electrode [22].

While there is a decrease in peak current and shifts in peak positions, no significant deviation in the overall shape of the voltammograms was observed after 10 cycles, indicating that the QRE-Na electrode remains relatively stable over time.

V. Conclusion

A comparative analysis of three different fabrication methods for planar quasi-reference electrodes (Ag/AgCl) on PCBs is presented. Our findings indicate that the chlorination of silver using sodium hypochlorite gives the best results in terms of electrode drift over time. These results highlight the potential of PCB-based fabrication for producing reliable, cost-effective reference electrodes suitable for portable biosensing applications. Future work involves integrating the electrodes into complete biosensing systems.

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