Electrochemical Sensors with Screen Printed Ag|AgCl|KCl Reference Electrodes

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***Abstract*—This paper presents the printed thick film Ag|AgCl|KCl reference electrodes for electrochemical or biosensors application and their electrochemical and analytical performance. The reference electrode exhibits a stable potential against standard glass reference electrode with a potential difference of 5 mV in the deionized water. The anodic and cathodic peak current of the electrode increase with the increase in scan rate in the range of 25-150 mVs^{-1}. The open circuit potential response of thick film reference electrode in the NaCl concentrations range (30-100 mM) was measured and it shows a stable potential in each test solution. The fabricated reference electrode shows an excellent application for an electrochemical pH sensor.**

Keywords—Reference electrode, Thick film, cyclic voltammetry, potentiometric, KCl layer

I. INTRODUCTION (*Heading 1*)

Reference electrode (RE) with a stable potential is necessary in majority of electrochemical studies such as potentiometry, cyclic voltammetry, and electrochemical impedance spectroscopy to complete an electrochemical cell. For example, RE serves as a counter electrode to complete the circuitry in potentiometric sensors. The Ag|AgCl based electrode is one of the most frequently used RE among many which include $Hg|Hg_2Cl_2$, $Cu|CuSO_4$ or, and Hg|HgO based REs [1,2]. The major advantages of Ag|AgCl based RE are its stable potential within an ionic concentration of solution and simple fabrication. Conventional Ag|AgCl is a glass based electrode and consists of an Ag wire coated with AgCl and immersed in a saturated KCl solution. However, this is incompatible with many applications such as flexible/wearable electrochemical biosensors where there is need for miniaturized devices, and other applications where high pressure and high temperature operation is desired. The glass based REs are also unsuitable for biosensors, used to monitor food (e.g. meat) quality as there is high risk of broken glass fragments leftover in the food. For this reason, recently the miniaturized thick film Ag|AgCl based RE have started to attract the attention [3-6]. Screen printing has been used in many of these works as a simple fabrication process [7, 8].

The major requirements to be fulfilled when miniaturizing RE are: the RE must have a stable potential (i.e the potential in this electrode is not affected by the composition in which it is present), the potential should establish reversibly (i.e. the potential in the RE should be recovered after a perturbation of the system) and the potential should be reproducible (i.e. the same potential is measured with the same type of electrode under the same experimental conditions) [9]. In REs, KCl plays a crucial role. In order to stabilize AgCl concentration in the RE, typically a KCl solution is utilized [10]. However, the thick film containing pure KCl easily dissolves in water and leads to the potential becoming unstable. To avoid this, glassy-KCl and polymer-KCl layers have been reported in literature [3-6]. Furthermore, the influence of hydration port (part of KCl layer directly in contact with the solution) and sealant used for waterproofing on the RE performance has been investigated [3-5]. However, the influence of the thickness of KCl layer on performance and lifetime of RE has been not be studied well.

In this work, we present a new glass-KCl layer composition. The layer was printed on various substrates including alumina and low temperature co-fired ceramics (LTCC) [10, 11]. The printed planar RE shows very good performances for pH sensor use. In this work, the influence of the KCl layer thickness on the hydration and potential response performance of thick film RE has been studied. A detailed analytical study and the performance of the printed RE with different Cl^- ion concentration was also carried out. Finally, the RE performance with an electrochemical sensor in the range of pH 5-9, which is important for biomedical, food quality and water pollution monitoring application have been discussed. The fabricated electrode reveals excellent sensing performance in potentiometric, electrochemical impedance spectroscopic and amperometric applications.

II. EXPERIMENTAL SECTION

A. Fabrication of Reference Electrode

The schematic representation of the fabrication is shown in Figure1a. The fabrication steps of the Ag/AgCl/KCl RE were based on our previous works [10, 11]. Fig. 1b shows the schematic diagram of the cross-section of the RE. The comparison of thick film RE with glass RE is shown in Fig.1c. In a RE, KCl layer plays an important role and functions as ionic conducting path between Ag/AgCl electrode and the electrolyte. In this work, we used a lead-free glass powder-KCl composite as a KCl layer for RE [10]. This KCl layer (salt matrix) was screen printed on top of AgCl layer. To check the influence of performance of this KCl on potential stability and hydration response, we printed the layer on different thickness (~10, 20 and 30 µm). The fabricated RE presents a miniaturized size in comparison to the commercial glass RE as shown in Fig.1c.

B. Electrochemical measurements and Characterization

The electrochemical performances of the thick film RE, were evaluated using cyclic voltammetry (CV) and potentiometric methods in a three and two-electrode cell system by using Metrohm Autolab. To check the proper operation of the RE, the potential difference (emf) between this RE with a commercial glass RE (Sigma Aldrich, UK) was measured by dipping the electrodes in deionized water. The hydration time, time to reach a stable potential, was initially measured for thick film REs with the glass RE. The CV analysis was carried out

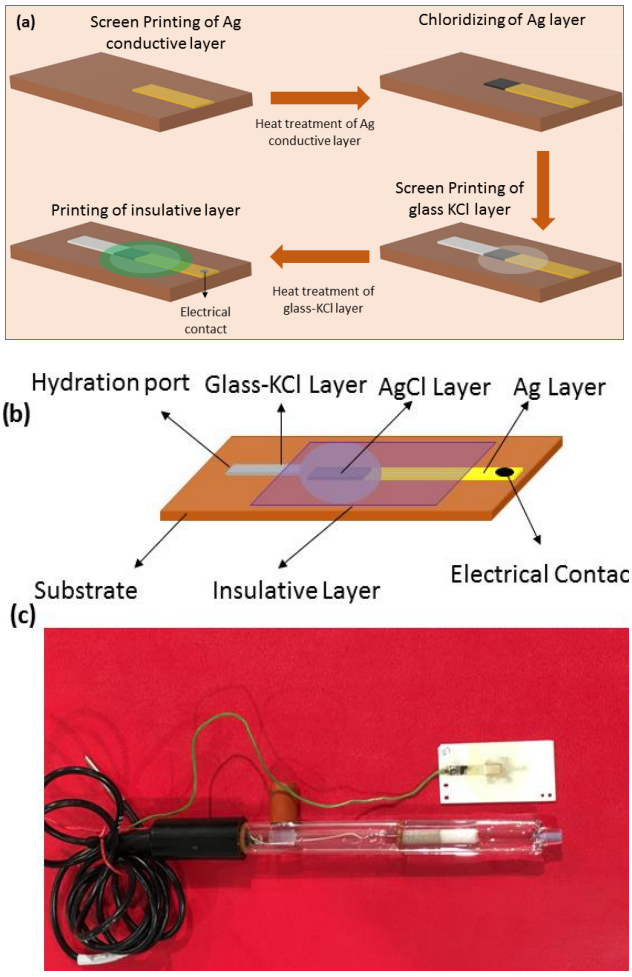

Fig. 1: (a) Schematic representation of fabrication of thick film reference electrode (b) Cross-sectional view of reference electrode with different layers and (c) image represent the comparison of thick film and commercial glass based reference electrode.

with a 3 M KCl concentrated solution by varying the scan rate from 25-150 mV/s between +1 to -1V. For checking the analytical performance of the prepared RE, the open circuit potential (OCP) was measured against glass RE and counter platinum electrode with different Cl- concentration. The Cl^- ion concentration of the solution was varied by dropwise addition of NaCl in the range of 30-100 mM. The sensing performance of the developed RE has been demonstrated by using pH sensing electrode based on RuO_2. All measurements were carried out at room temperature.

III. Results and Discussion

Figure 2a represents the initial response of the thick film RE with a thickness of KCl layer~10µm. The potential difference of the fabricated thick film RE versus the glass RE predicts that initially, the potential was not stable due to the hydration response of the KCl layer. We found that during the first 3 h. the electrode was unstable and presented a high noise signal during the first measurement. So, after fabrication of the electrode, prior to measuring, for the proper functioning ion conductive KCl channel, it is necessary to keep the RE in test electrolyte. After hydration time, the potential difference between these two reference electrodes was stabilized close to zero, implying a proper working condition of the fabricated thick film RE. One of the major advantages of this thick film RE is that after measurement, the RE can be kept in a dry atmosphere. However, before doing the next measurement, the thick film RE needs a preliminary period (nearly 20 min) to form a stable potential in solution. This time is needed to the function of the ion conducting KCl channel in the solution.

In thick film RE, the composition of the salt matrix layer and the hydration port dimensions influence the hydration response, potential and lifetime of the RE [3]. It was found that the glassy-KCl matrix showed faster stability than polymer-KCl matrix [3]. The observed hydration time (20 min, after initial stabilization) of the prepared RE was comparable with those reported thick film REs [3,4]. Fig. 2b represents the influence of the thickness of the KCl layer on the performance of thick film RE. During the initial period of measurement, it was found that with increasing thickness of layer the magnitude of the measured potential was increasing. This may be caused by a lower mobility of ions in the glass KCl matrix due to an increased electrode thickness. However, after continuous long term measurements, the measured potential of 30 µm thick KCl layer RE was dropped from 11 mV to 5mV due to the loss of salt matrix while reacting with the solution. The performance of the thick film RE (KCl layer of 30 µm) was measured after 2 years (stored in dry conditions) and it shows a stable potential of 5 mV against glass RE. The performance of this RE (KCl layer 30µm) was investigated by using CV analysis after long time measurement.

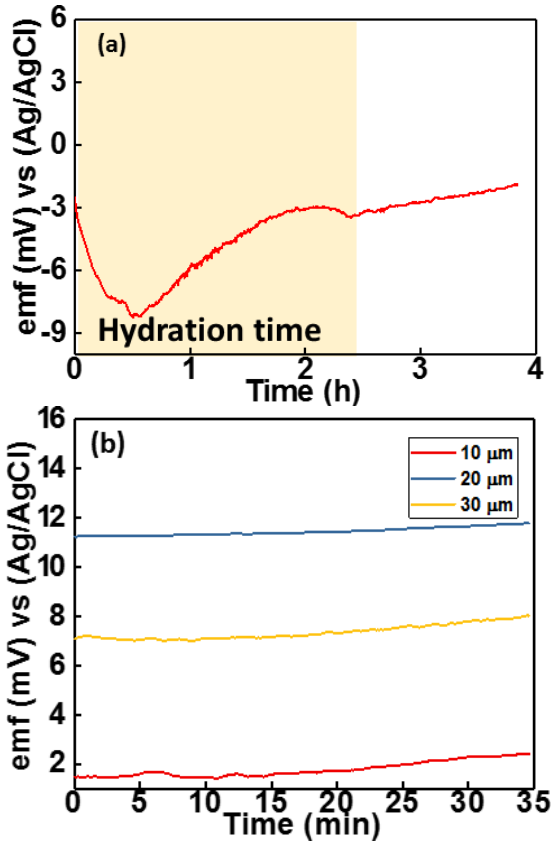

Fig. 2: (a) Hydration response of the thick film RE (b) emf between the thick film RE of different KCl layer thickness with the glass RE.

CV is a non-destructive transient electrochemical technique of micro-electrolysis, where the electroactive species reaches the electrode by diffusion. In this method, a potential ramp, which is changed linearly in time, is applied over the working electrode. Figure 3a represents the CV spectrum of planar thick film RE against glass RE in 3 M KCl solution with scan rate between 25-150 mV/s. It was found that the anodic and cathodic peak current increased with an increase in scan rate. The variation of peak currents with scan rate is shown in the inset of Fig.3a. Moreover, it was observed that the potential corresponding to each scan rate was slightly shifting with an increase in scan rate. The shift in potential is due to the quasi-reversible redox reaction at high scan rate [12].

On the other hand, the OCP or zero current potential is the measured potential value when a high impedance is placed across an electrochemical cell, thus, no appreciable current flows through the system. Fig. 3b represents OCP of thick film RE for different concentration (30-100 mM) of NaCl solution. It was observed that in each solution the OCP of the electrode was almost stable after an initial drift. Knowing the OCP value will further help to determine the ionic concentration in a solution through a calibration curve. In our previous work, we successfully demonstrated the pH sensing performance of the thick film RE against RuO_2 based pH-sensitive electrode. In the range of pH 2-11, the sensor showed a sensitivity of 58 mV/pH [11]. As a future application of the sensor in the biomedical, food processing and water pollution monitoring, we observed that the thick-film pH sensors showed a sensitivity of 55 mV/pH in the pH range 5-9. For healthcare application especially for sweat analysis (monitoring of pH, glucose and Cl^- ion concentration) a flexible RE will be fabricated based on same method by using low temprature firable AgCl and KCl pastes.

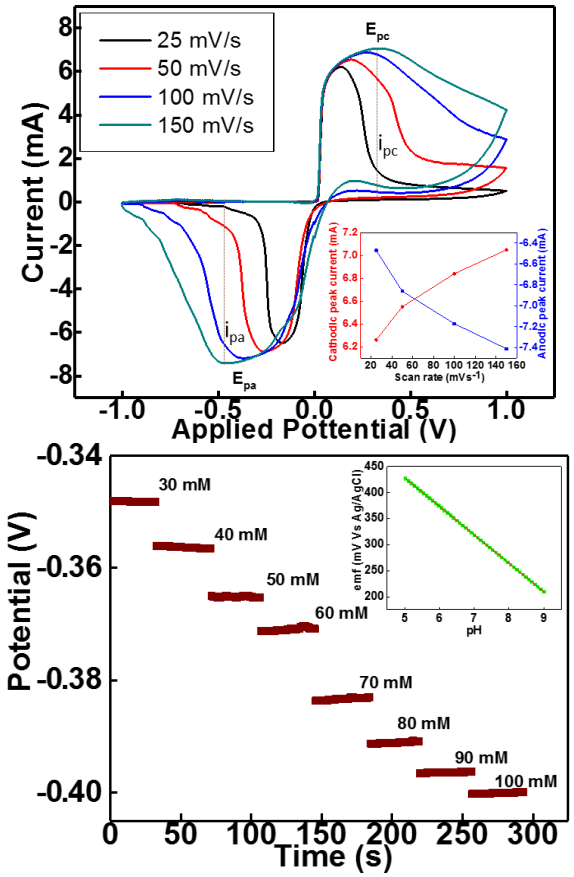

Fig. 3: (a) Cyclic voltammetric response of thick film reference electrode (inset: peak currents vs scan rate) (b) Potential response of thick film RE against a glass Ag/AgCl RE to different NaCl concentrations of solution (inset pH sensing performance).

IV. Conclusion

This paper presents the electrochemical performance of a printed thick film Ag|AgCl|KCl reference electrode which has significant importance in electrochemical or biosensors application. It was found that the thickness of KCl layer in thick film reference electrode had strong influences in the initial stabilization of the reference electrode. The fabricated planar reference electrode with a thickness of ~10µm showed a stable potential and close to zero against glass reference electrode. This implies the excellent performance of the planar reference electrode. The planar reference electrode exhibited excellent application as a pH sensor. Followed by this work, the next aim is the fabrication of a flexible reference electrode for wearable systems for healthcare applications.

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