



The effect on performance of fabrication parameter variations of thick-film screen printed silver/silver chloride potentiometric reference electrodes

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ABSTRACT

Thick-film screen printed silver–silver chloride (Ag/AgCl) reference electrodes have been fabricated and investigated as an alternative to liquid electrolyte Ag/AgCl reference electrodes. The performance of the electrodes was examined with variations of the potassium chloride (KCl) concentration in the final (top) layer of the electrode. Also, different types of binder (glass and polymer) were tested for the underlying Ag/AgCl layer. The addition of another layer on top of the KCl containing salt matrix layer has been found to provide a better stability in varying concentrations of KCl test solutions. The electrodes were found to give a satisfactory performance when tested for stability in different pH solutions.

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1. Introduction

There has been a growing interest in the development of new, miniaturised and low cost electrochemical sensors suitable for industrial, biomedical and environmental applications [1–3]. Thick film technologies together with electrochemical methods embrace the requirements for these devices by giving cost competitive solutions for the fabrication of compact, rugged and robust systems [1]. Thick film chemical sensors offer alternative solutions and allow flexible design with a wide range of materials, low cost infrastructure and mass production capability [4–8].

The response of any electrochemical potentiometric electrode is meaningless without a reference electrode against which comparisons can be made [9]. There are several types of reference electrodes such as the standard hydrogen electrode and saturated calomel electrode. Most of those electrodes are far too complex to be used outside of the laboratory environment while others, in case of breakage, are harmful to the environment. The silver/silver chloride (Ag/AgCl) reference electrode is a reference electrode of the ‘second kind’ [10] and is the simplest and most practical type of reference electrode used in industry and research and it has no significant environmental issues in use. Most commercially

available Ag/AgCl reference electrodes are of the fragile and expensive conventional type of electrolyte-filled devices. Conventional gel-filled electrodes are unusable in applications where robustness and miniaturisation are of high importance. Also, in applications of high electrode density, the cost of such an electrode is a major restriction. The thick-film devices reported here are approximately ten times cheaper and are implemented on the same principle as the conventional electrolyte-filled Ag/AgCl reference electrode. They attempt to mimic its operation through the immobilisation of salt reservoirs in the form of salt matrix layers fabricated as upper layers of a planar design that are in contact with the analyte [11].

The conventional commercial silver/silver chloride reference electrode has a relatively simple construction (Fig. 1). It consists of a silver metal electrode coated with silver chloride which is immersed in a saturated filling solution and enclosed in a glass or plastic tube separated from the test solution via a porous plug [12]. The typical planar structure of the thick film equivalent (Fig. 1) consists of a silver back contact, a waterproofing layer, a silver/silver chloride interfacial layer and one or more overlapping salt matrix layers containing typically potassium chloride (KCl) powder in a lower layer and potassium nitrate (KNO₃) powder in an upper layer. This double layer approach mimics the double junction type of liquid electrolyte reference electrode that typically contains two liquid electrolytes separated by a porous plug.

The research reported here investigates variation of the fabrication parameters of screen-printed thick-film Ag/AgCl reference electrodes, such as salt concentration, layer thickness and interfacial layer material types, and their effect on sensor characteristics. The monitoring of electrode potentials in different test solutions

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Fig. 1. Comparison of commercial liquid-filled (top) and screen-printed (bottom) reference electrodes, shown on same scale. The thick-film device shown is less than two times smaller in length and only a couple of millimetres thick, but can be miniaturised much further to only a few millimetres square if desired.

over time has been used as a method to determine hydration times, drift rates, stability and useful lifetime of the devices. A major aspect of the investigation has been the focus on the electrode stability and response time across different ionic concentration solutions arising from the addition of different types of salt containing outer layers. The results contribute towards optimisation of the fabrication parameters of low cost miniaturised screen-printed Ag/AgCl reference electrodes and demonstrate the feasibility of the development of a miniaturised alternative to the commercially available liquid electrolyte filled Ag/AgCl reference electrode through the use of thick-film technology.

The classic commercially available silver/silver chloride reference electrode typically consists of a silver wire coated with silver chloride and surrounded by a saturated solution of KCl (approximately 3.5 M) [10]. The silver/silver chloride layer forms the interaction between the ion movement in the KCl solution and the electron movement in the silver wire. In the idealised system the internal element is at equilibrium:



The equilibrium potential (E) of the electrode is defined by the Nernst equation:

$$E = E^\theta + \frac{RT}{nF} \ln \frac{a_{\text{oxi}}}{a_{\text{red}}} \quad (2)$$

where E^θ is the standard potential (V); R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); T is the absolute temperature (K); n is the number of moles of electrons transferred in the reaction; F is the Faraday constant ($96,485 \text{ C mol}^{-1}$); a is the activity; oxi is the oxidant and red is the reductant. In the case of the Ag/AgCl electrode (2) can be re-written as:

$$E = E^\theta + \frac{RT}{nF} \ln \frac{a_{\text{AgCl}}}{a_{\text{Ag}} a_{\text{Cl}^-}} \quad (3)$$

The activity of a species a , is defined as the product of the activity coefficient of the specific substance and its concentration. When the species is at its standard state the activity coefficient can be approximated to 1. In the case of AgCl and Ag since they are in the solid state, their activity can be equated to their concentrations therefore Eq. (3) can be expressed as:

$$E = E^\theta - \frac{RT}{nF} \ln(a_{\text{Cl}^-}) + \frac{RT}{nF} \ln \frac{\text{AgCl}}{\text{Ag}} \quad (4)$$

The Nernst equation for a cell at a nominal room temperature of 25°C is frequently expressed in terms of base 10 logarithms, with numerical values replacing the constant coefficients and hence re-writing Eq. (4) gives:

$$E = E^\theta - 0.592 \log | \text{Cl}^- | + 0.0592 \log(k) \quad (5)$$

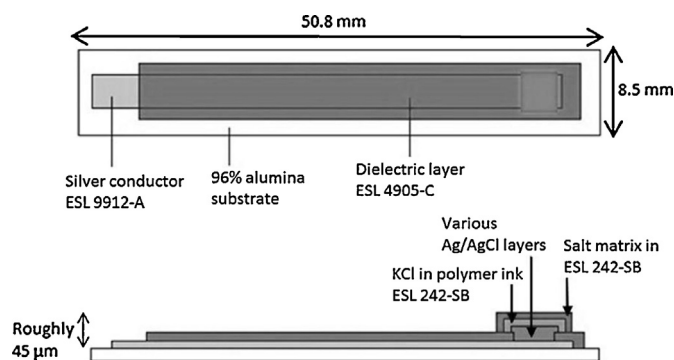


Fig. 2. The construction of a typical screen-printed Ag/AgCl reference electrode.

where k is the concentration ratio of Ag to AgCl. The measured electrode is said to display Nernstian behaviour when its potential (E) decreases by approximately 59 mV for every decade change in chloride ion concentration at 25°C and provided that the activity coefficient of chloride ion in the solution is approximately equal to unity. AgCl is a sparingly soluble salt therefore the surrounding KCl solution will become saturated very quickly, which keeps the AgCl activity constant regardless of the solution into which the electrode is immersed. The activity of Ag is controlled by the activity solubility product, which is invariant at a certain temperature whilst the activity solubility product is the product of the silver ion activity and the chloride ion activity and hence the potential of the electrode depends only on the chloride ion activity of the KCl solution surrounding the electrode.

2. Fabrication process

The construction procedure described below is designed to mimic the construction of a single junction electrolyte-filled commercial reference electrode. Double junction electrolyte-filled reference electrodes are generally found to be more stable and more reliable in time, so in an attempt to improve the stability of the thick-film electrodes, some double junction thick-film reference electrodes were also fabricated. The only difference of double junction to single junction electrodes is that another layer containing KNO_3 was printed on top of the polymer/KCl layer (Fig. 2).

The electrodes were screen printed onto $50 \text{ mm} \times 50 \text{ mm}$, 0.625 mm thick, 96% alumina substrates (Coorstech). Each substrate was divided into six equal sized electrodes and prescribed with laser lines so that individual electrodes could be easily snapped off along those lines. Therefore, a simultaneous six electrode fabrication was possible as shown in Fig. 3.

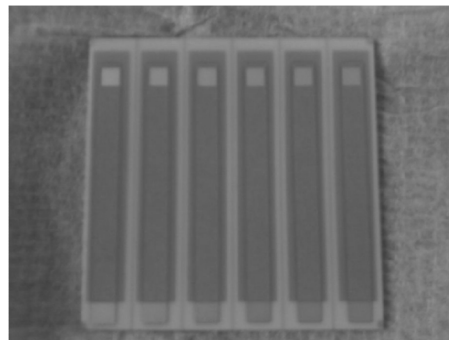


Fig. 3. Six simultaneously fabricated reference electrode test strips on a $50 \text{ mm} \times 50 \text{ mm}$ alumina substrate, only the first two layers are present in this case. Simultaneous fabrication of the electrodes can significantly lower the cost while increasing the speed of manufacture.

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