Design and Fabrication of Low Cost Thick Film pH Sensor using Silver Chlorinated Reference Electrodes with Integrated Temperature Sensor

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Abstract. This paper describes the design and fabrication of thick film pH sensor, in which the reference electrode has been formed by chlorination of Ag using FeCl₃. The process was aimed to replace Ag/AgCl paste commonly used as reference electrodes. Fabricated using thick film screen printing technology on Al₂O₃ substrate, the pH sensor showed a measured sensitivity of -52.97, -53.17 and -53.68 mV/pH at 25 °C, 45 °C, and 65 °C, respectively. The measured values were close to the theoretical Nernstian slope of -59 mV/pH 25 °C. The sensor was also designed with an integrated Ruthenium based temperature sensor for future temperature compensation. The measured resistance temperature characteristics showed a linear response over the range of 25 – 80 °C. This miniaturised planar sensor should find wide application, especially in field water quality monitoring, replacing their glass type counterparts.

1 Introduction

Nowadays, water quality monitoring requires real time data in which measurement must be performed in situ/online from a remote location. River monitoring, marine, aquaculture, agriculture, and mining are among the areas where online water quality monitoring have been widely implemented [1-4]. Sensors employed in such application thus need to be compact, rugged and robust to withstand harse environmental condition. Thick film technology offers the possibility of fabricating sensors on planar substrates using wide selection of materials, resulting in miniature devices at low fabrication cost [5].

One parameter of interest in water quality monitoring is pH. As a measure of the acidity and alkalinity of water, the role of pH in controlling the aquatic life in water is very important [6]. One of the most common techniques in pH determination is by using electrochemical sensors, where a pair of electrodes are compared for their potentiometric responses. One of the electrodes serves as a reference and the other serves as a working electrode. Usually, materials used for reference electrodes are Ag/AgCl, due to their stability, performance, and safety against environmental issues [7].

In today’s pH electrochemical sensors, however, the relatively high cost of Ag/AgCl reference electrode material [8] has become a problem that needs to be solved either by replacing with different material, or by finding an alternative method for its preparation. In addition, the variation of pH values against temperatures [9] has made the sensor fabrication increases due to the need for a temperature compensation circuit.

In attempts to improve the performance of a pH sensor, previous works have included fabrication of Ag/AgCl electrode using screen printing technique [10-12], deposition by electrochemical process of Ag and AgCl onto graphite [13], the use of various metal oxides as pH electrodes [14-17], and the application of nanotube based electrodes [18]. Although some materials have proved to be a good candidate for pH reference electrode, however, none of the methods has yet produced a satisfactory cost over performance results.

This research offers a method by which Ag/AgCl reference electrode can be produced by chlorination of Ag using FeCl₃, resulting in a sensitive pH reference electrode. Fabricated using thick film technology, a pH sensor integrated with Ruthenium based temperature sensor can be batch fabricated on Al₂O₃ substrate. This paper will describe the design, fabrication, and the results of characterisation of the sensor.

2 Design and fabrication

The sensor device has been designed to fit on a 10 x 25 mm alumina (Al₂O₃) substrate. Device dimension was optimised to allow for ten devices to be simultaneously fabricated on a 50 x 50 mm Al₂O₃ substrate. As shown in Figure 1, the structure consists of Ag/AgCl reference electrode, AgPd working electrode, KCl electrolyte, Ruthenium based active layer and temperature sensor, and dielectric passivation layer. The use of Ruthenium as an active layer for pH sensor has been demonstrated [19] in the previous work. The minimum linewidth and spacing for the conductive electrode tracks and resistive temperature sensor are 300 μm and 500 μm, respectively.
The solder pads were designed as 2 x 2 mm each size, and all the structures are contained within 0.8 mm from the edges of the substrate to allow for safety when the cutting is done manually using diamond scrubber.

Fabrication of the sensor device was started by screen printing AgPd conductor paste (ESL ElectroScience) used as electrodes on a 50 x 50 mm, 96% Al₂O₃ substrate. After printing, the tracks were dried at 100 °C for 5 min, followed by cooling at room temperature. The second step was screen printing a Ruthenium Dioxide (ESL ElectroScience) resistor paste used as the active layer of the working electrode and the temperature sensor. The resulting structure was then fired using conveyor belt furnace for 45 min with a peak temperature of 850 °C. Figure 2 shows the resulting structure after firing process.

Passivation of the conductor and resistor tracks was done by screen printing a dielectric layer (ESL ElectroScience 4608), followed by drying at 100 °C for 5 min. To form a Ag/AgCl reference electrode, the top side of the AgPd conductor track was printed with an Ag paste (ESL ElectroScience), followed by drying at 100 °C for 15 min. Chlorination of the Ag layer was done by dipping the chip into 0.05 M FeCl₃ solution for 50 s and then rinsing in a deionised (DI) water. As has been demonstrated previously [20], this technique should produce a fast and uniform coating of AgCl having particle sizes in the order of nanometer. The immersion of Ag inside FeCl₃ solution produces AgCl according to the following reaction:

\[ \text{Ag} + \text{FeCl}_3 \rightarrow \text{AgCl} + \text{FeCl}_2 \]  

Layer of homogeneous AgCl should form at the surface of the Ag layer forming Ag/AgCl reference electrode.

The final step in the formation of the reference electrode was to apply a KCl electrolyte layer over the Ag/AgCl layer. A 3.5 M KCl solution was prepared from 15.65 g crystalite KCl, added by 60 ml water. Magnetic stirring at room temperature for 15 min was done and 7% (by weight) of gellatine was added to the mixture to increase the adhesivity of the KCl solution. The Ag/AgCl electrode layer was then dipped into the KCl mixture for 1 min, and then dried at 100 °C for 5 min. Figure 3 shows the final device structure.

Device characterisation was performed in two steps. Firstly, the temperature sensor was characterised to find their resistance temperature characteristics. The aim was to find a linear relationship that will be used for constructing a temperature compensation circuit in the future. As such, several devices were cycled through various temperatures ranging from 25 – 80 °C using hotplate, and the resulting changes in resistance values.

**Figure 1.** The structure of thick film based pH and temperature sensors designed on a 10 x 25 mm alumina substrate: [1]. Alumina substrate (Al₂O₃), [2]. Working Electrode (AgPd), [3]. Temperature Sensor (RuO₂), [4]. Dielectric, [5]. Active layer (RuO₂), [6]. Reference Electrode (Ag/AgCl), [7]. Electrolyte (KCl).

**Figure 2.** The resulting screen printed conductor AgPd and resistor RuO₂ tracks after firing process.

**Figure 3.** Final device structure after formation of KCl layer over Ag/AgCl reference electrode.

**Figure 4.** Experimental setup for temperature sensor characterisation using a hotplate and a digital multimeter.

**3 Device characterisation**

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were measured directly between the two pads of the temperature sensor using a digital multimeter. The measurement temperature range was chosen as not to exceed the normal water condition during real application. The experimental setup for temperature sensor characterisation is shown in Figure 4.

The second characterisation was performed to study the response of the pH sensor against various pH solutions at various temperatures. The sensor response was measured in terms of its potential difference between the reference and working electrodes while exposed to a known pH solution. For this purpose, solutions having pH values of 2.5, 5.5, 9.5, and 11.5 have been prepared using Kangen Water®. As a comparison, the potential difference of these solutions were measured using commercial pH meter (Lutron YK-2005WA) prior to performing the sensor characterisation.

4 Results and analysis

4.1 Ruthenium based temperature sensor

Figure 5 shows a typical response of resistance changes against temperature variation from three RuO$_2$ based temperature sensors. It must be noted that although batch fabricated, each sensor should show slight variation in their characteristics, and thus analysis must be done on each individual device. The aim of temperature sensor characterisation was to find a linear relationship between resistance and temperature, such that

$$ R_T = R_0 (1 + \alpha \Delta T) $$

where $R_T$ is resistance at temperature $T$, $R_0$ is resistance at reference temperature, and $\alpha$ is the temperature coefficient of resistance of the RuO$_2$ material. Equation (2) is represented by the linear trend line for each sensor data set, and if the reference temperature is taken at 0 °C, therefore $R_0 \alpha$ is the same as the gradient and $R_0$ is the constant value of the trendline equation.

Table 1 summarises the values of $R_0$ and $\alpha$ for three RuO$_2$ based temperature sensors

<table>
<thead>
<tr>
<th>Chip #</th>
<th>$R_0$ (kOhm)</th>
<th>$\alpha$ (1/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.551</td>
<td>0.009501</td>
</tr>
<tr>
<td>B</td>
<td>1.481</td>
<td>0.005262</td>
</tr>
<tr>
<td>C</td>
<td>1.310</td>
<td>0.011227</td>
</tr>
</tbody>
</table>

4.2 The pH sensor

The response of the pH sensor under various known pH solutions at temperature 25 °C is displayed in Figure 6. It can be seen that for acid solutions (low pH values) the sensor exhibits a net positive potential difference, whereas for base solutions (high pH values) the sensor shows a net negative response. This means that the response behaves according to the Nernstian equation:

$$ E - E_0 = -0.05916 \text{ pH} $$

where $E - E_0$ is the measured potential difference of the pH sensor. The slope of the linear trendline generated by the graph is -52.97 mV/pH, which shows the sensitivity of the fabricated sensor.

As a comparison, also in Figure 6 it is shown the measured potential difference of the solutions taken using commercial pH meter. The meter has a measured sensitivity of -56 mV/pH. The minor difference indicated that the chlorinated Ag/AgCl reference electrode can serves as an alternative to the commercially available Ag/AgCl pastes.
Figure 7 shows the dynamic response of the sensor at 25 °C, expressed in terms of their potential values against time. It can be seen that the time it takes to get a stable response varies from 10 min (from pH 2.5 to pH 5.5), to 5 min (from pH 5.5 to pH 9.5) to 3 min (from pH 9.5 to pH 11.5).

The effect of temperature variations from 25 to 65 °C on the sensor response is shown in Figure 8. The gradients of the linear trend line are -52.97, -53.17, and -53.68 mV/pH, for temperature of 25, 45, and 65 °C, respectively. As expected, the gradient increases with increasing temperature, although the increase is still lower than the ideal Nernstian slope at the corresponding temperature.

5 Conclusion

The design and fabrication of thick film pH sensor, integrated with a temperature sensor has been described in this paper. The main results indicated that the chlorination of Ag using FeCl₃ has produced a reference electrode, which, along with an RuO₂ active layer, is capable of detecting changes in pH solutions. In fact, at temperature of 25 °C, the sensor has a sensitivity of -52.97 mV/pH, which is close to the ideal Nernstian slope of -59 mV/pH. The pH sensor also showed an increasing sensitivity with increasing temperature of the solutions. The Ruthenium based temperature sensor showed a linear response over the temperature range of 25 – 80 °C. Although fabricated on the same substrate, the measured R₀ and α for the temperature sensor has indicated variation due to the nature of thick film processing technology.

To obtain the right pH reading, it is necessary that a temperature compensation circuit be developed in the future work.

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References


