Performance of miniaturised thick-film solid state pH sensors

M. Glanc-Gostkiewicz[a], M. Sophocleous[b], J.K. Atkinson[b], E. Garcia-Breijo[c]

[a,b]Faculty of Engineering and the Environment, University of Southampton,Southampton, SO17 1BJ, United Kingdom
[c]Instituto de Reconocimiento Molecular y Desarrollo Tecnológico,Universidad Politécnica de Valencia, Valencia, 46022 Spain

Abstract

The performance of novel solid state Thick-Film pH sensors for water quality sampling that are designed for deployment in remote catchment areas is described. These miniaturised screen printed planar pH sensors are an alternative to conventional glass pH electrodes that have many disadvantages such as high-cost, large size, mechanical fragility and limited shape. The approach adopted here for improvement of the ruggedness of the pH electrode is through its implementation as a screen printed metal oxide (RuO_2) ion selective electrode used in combination with a screen printed silver/silver chloride (Ag/AgCl) reference electrode. Various choices of materials have been evaluated for the fabrication of the Thick-Film pH sensors resulting in a device with a sensitivity of approximately 30mV/pH at ambient temperature.

1. Introduction

Rivers are the habitats for living organisms and any changes in the alkalinity or acidity of the water can be critical to the survival of aquatic life. Rivers have some capacity to prevent changes in pH by the structure and composition of the river bed; however drastic changes in pH can have very detrimental effects on river health.

Agricultural industry is a major user of water resources. It also contributes intensively to water pollution through processes such as the use of pesticides and fertilisers, and the spreading of slurries or manure. To detect the contamination of water courses, a network of upstream early warning systems consisting of in situ miniaturised electrochemical sensors is required as a simple alternative to the current methods of downstream detection of pollution in rivers [1]. This approach enables the localization of pollution sources and better control of the environment but requires large numbers of rugged devices suitable for wide scale field deployment. The cost implications of this approach render it unfeasible using conventional electrochemical devices.

Currently the most widely used technique for determination of pH in the laboratory is the glass bulb type pH electrode. This electrode is well-established because of its excellent performances with respect to slope, long-term stability, selectivity, detection limit, and insensitivity versus redox systems [2]. However this traditional glass electrode with an internal liquid reference system exhibits several drawbacks such as mechanical fragility, large size and high cost. Thick-Film technology can resolve these limitations through the fabrication of small, rugged and inexpensive devices which can mimic the commercially available pH electrode and reference electrode systems [3, 4]. Moreover it can implement a competitive solution to the current expensive environmental monitoring with pH devices by manufacturing sensors with Thick-Film processes where metal oxides can be used to implement the pH sensor active layer [2, 6].

In this paper an investigation, formulation and production process of these alternative thick film pH sensors are described. The devices described here were fabricated specifically for water catchment area monitoring using routine sample collection deployment alongside passive samplers, to provide better estimations of environmental concentrations and uptake rates of pollutants in water courses. The results described here arise from laboratory investigations prior to further investigations in field trials in order to validate their use for environmental sampling.

1.1 pH sensor theory

The pH of a solution can be determined by a potentiometric pH sensor where the potential difference between two electrodes, i.e. a pH sensitive electrode and a reference electrode, is measured. The reference electrode provides a stable constant reference potential regardless of the solution in which is immersed while the ion selective electrode responds to the change of the H^+ concentration in the solution.

The Thick Film pH sensors presented in this study consist of a Thick-Film Ruthenium Oxide ($RuO_2.xH_2O$) pH electrode (one type) and a Thick –Film Ag/AgCl reference electrodes (four types). They are implemented on the same principle as the conventional glass pH electrode and the single junction electrolyte-filled Ag/AgCl reference electrode by attempting to mimic their construction [7].
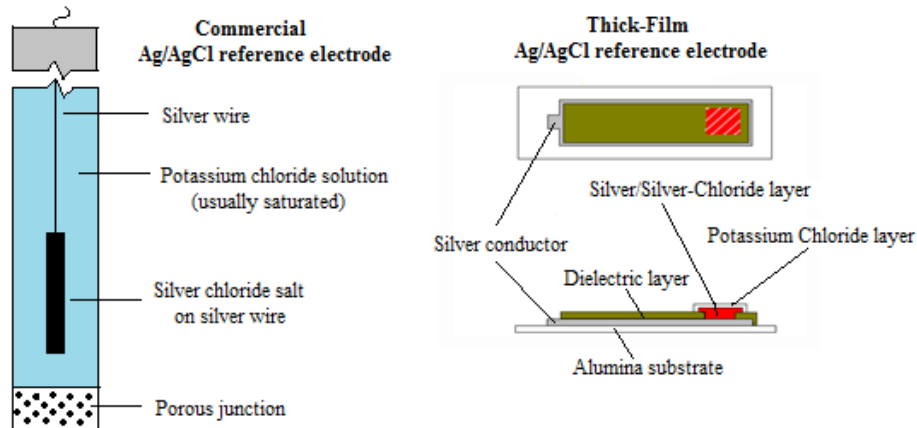

Fig 1. Commercial Ag/AgCl reference electrode (left) and Thick-Film Ag/AgCl reference electrode (right)
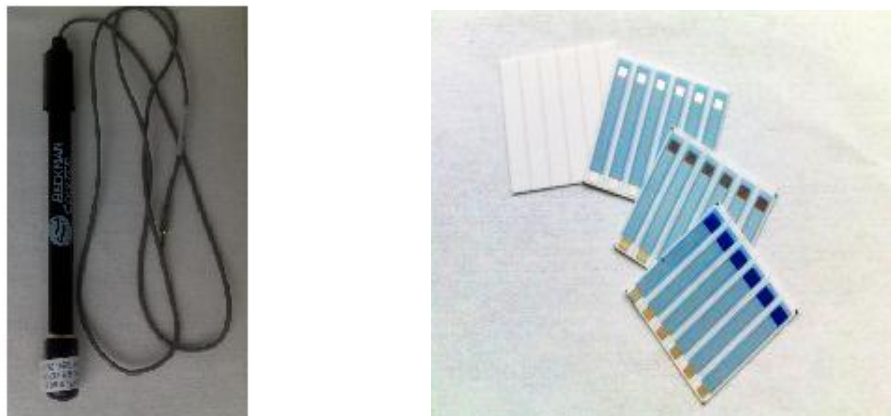

Fig 2. Commercial gel-filled reference electrode (Beckman Coulter A57193) (left) and Thick-film Ag/AgCl reference electrodes (right)

The common reference electrode used in pH measurements consists of a silver wire coated with silver chloride in a fill solution of potassium chloride (KCl). The Ag/AgCl electrode potential response is controlled by the following equilibrium reaction:

$$AgCl_{(s)} + e^- \leftrightarrow Ag_{(s)} + Cl^-_{(aq)}$$ (1)

Hence the equilibrium potential of the electrode can be expressed by the Nernst equation:

$$E = E^{\theta} + \left(\frac{RT}{nF}\right) ln \frac{(a_{AgCl})}{(a_{Ag} a_{Cl^-})} \tag{2}$$

where E^{θ} is the electrode's standard potential (V), T is the absolute temperature (K), R is the molar gas constant (8.31 J K^{-1} mol^{-1}), F is the Faraday constant (96485 C mol^{-1}), n is the number of electrons involved in the reaction, a_x is the activity of species x (where x is either AgCl, Ag or Cl$^-$).

The Nernst equation for a cell at a nominal room temperature of 25°C is frequently expressed in terms of base 10 logarithms:

$$E = E^{\theta} - 0.0592 \, log|Cl^-| + 0.0592 \log (k) \tag{3}$$

where k is the ratio of the concentrations of silver chloride to silver. The electrode demonstrates Nernstian behaviour when the measured electrode potential decreases by 59 mV for every decade change in chloride ion concentration at a room temperature of 25˚C. The measured electrode potential can also yield alterations due to changes in the ratio of silver chloride to silver (k).

Fog and Buck proposed and discussed five different possible explanations of the pH response mechanisms of metal oxides and suggested that the most probable theory was that of oxygen intercalation [5, 8, 9]. This mechanism is represented by the equilibrium reaction:

$$MO_x + 2\delta H^+ + 2\delta e^- \leftrightarrow MO_{x-\delta} + \delta H_2 O \tag{4}$$

where MO_x is a higher metal oxide and $MO_{x-\delta}$ is a lower metal oxide. The electrode potential for this reaction is given by:

$$E = \frac{RT}{F} ln \, a_{H^+}^1 + \frac{RT}{2F} ln \, a_O^s + constant \tag{5}$$

where $a_{H^+}^1$ is the proton activity in the liquid phase and a_O^s is the oxygen activity in the solid phase.

McMurray et al. [9], used The Pourbaix Atlas to present another mechanism of only one redox equilibrium between two insoluble ruthenium oxides:

$$RuO_2 + 2H_2O + H^+ + e^- \leftrightarrow H_2O + Ru(OH)_3 \tag{6}$$

The reaction potential being expressed by:

$$E = E_0 - 0.0591 \, pH \tag{7}$$

Assuming a near constant activity of the metal oxide, both of these mechanisms predict a Nernstian response of approximately -59mV per pH at ambient temperature (25°C).

2. Experimental details

2.1 Electrode fabrication

The studied electrodes were screen printed onto 96% alumina substrates (Coorstech) through successive layer deposition. An economical design of each sensor type permitted the simultaneous fabrication of six electrodes on a single, laser prescribed substrate, as shown in Fig. 2. The details of the component materials have been documented previously [5, 7]. The electrode types used in the experimental setup and their basic structures are shown in Fig. 3.

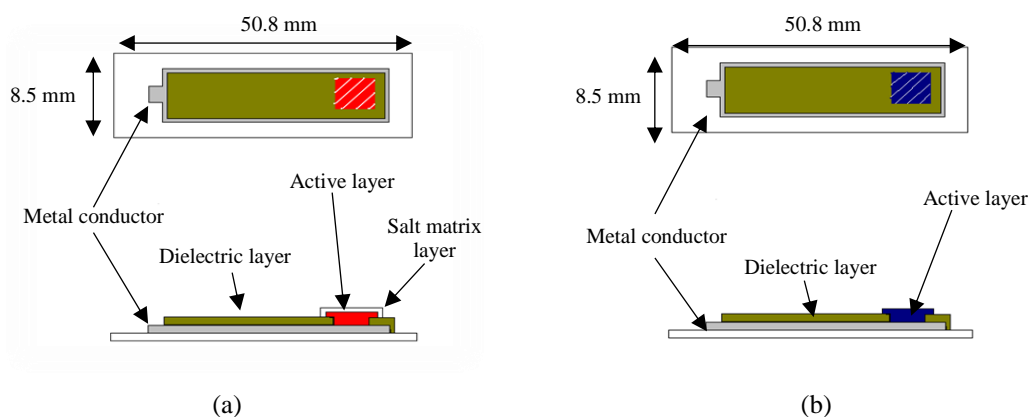| (a) | (b) |

Fig. 3. (a) Thick-Film reference electrode cross-section; (b) Thick-Film pH ion selective electrode cross-section

The tested devices varied in terms of their electrode active layer construction (Table 1). The same polymer bound Ag/AgCl layer (GEM C61003P7) was use for two types of reference electrodes. However, the 'Fired' Polymer Ag/AgCl electrodes were passed through a furnace at 850°C and, as suggested by the results of an SEM scan, a thin layer of Ag/AgCl was subsequently formed on top of the underlying Ag conductor. Two further types of Thick-Film reference electrodes were tested that do not possess a printed Ag/AgCl layer but instead have a thin layer of AgCl that was chemically grown on the Ag conductor.

Table 1. Types of electrodes with details of the component materials

Electrode type	Conductor layer	Waterproofing layer	Active Layer	Salt matrix layer
Bare Ag	Silver ESL 9912 A	Glass Dielectric ESL 4905 CH	-	-
Reference electrodes				
Polymer Ag/AgCl	Silver ESL 9912 A	Glass Dielectric ESL 4905 CH	Silver/Silver Chloride Paste GEM C61003P7	Polymer ESL 242 SB + 20% KCl powder
Fired Polymer Ag/AgCl	Silver ESL 9912 A	Glass Dielectric ESL 4905 CH	Fired Silver/Silver Chloride Paste GEM C61003P7	Polymer ESL 242 SB + 20% KCl powder
Chemically grown Cl layer 2min	Silver ESL 9912 A	Glass Dielectric ESL 4905 CH	*	Polymer ESL 242 SB + 20% KCl powder
Chemically grown Cl layer 1hr	Silver ESL 9912 A	Glass Dielectric ESL 4905 CH	*	Polymer ESL 242 SB + 20% KCl powder
pH ion selective electrode				
pH electrode	Platinum Gold ESL 5837	Polymer Dielectric GEM 2020823D2	Ruthenium Polymer Paste C50502D7	-

* An exposed silver window was chemically coated with a thin layer of silver chloride by electroplating in 1M HCl.

2.2 Experimental setup

The whole experiment was divided in two parts. Firstly the performance of the Thick-Film reference electrodes was ascertained through sequential testing in different strength KCl solutions. Subsequently a group

of the same type of reference electrodes was simultaneously examined with Thick-Film pH electrode in pH buffer solutions in a solution sequence of pH7, 10, 7, 4, 7, 4, 7, 10 and 7.

The KCl test solutions were made by dissolving KCl salt in de-ionised water until the solution reached saturation (Sat KCl solution). All the other solutions were made by diluting the saturated solution in the ratios of one tenth (1:10 Sat KCl), one hundredth (1:100 Sat KCl) and one thousandth (1:1000 Sat KCl). The Thick-Film sensors were initially hydrated overnight in 1:100 Sat KCl solution and subsequently cycled through the test solutions. The electrode potentials were measured with respect to a commercial gel-filled reference electrode (Beckman Coulter A57193) located centrally within a beaker containing the test solution and surrounded by the Thick-Film electrodes under test. All solutions were stirred using a magnetic stirrer. The test set-up is shown in Fig. 4. The electrodes were connected to a custom designed voltmeter and the experimental data were recorded in 5 seconds intervals with a portable data logger designed and constructed at Universidad Politécnica de Valencia and shown in Fig.5.
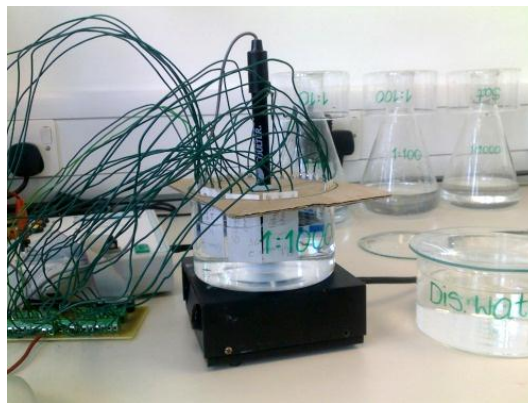

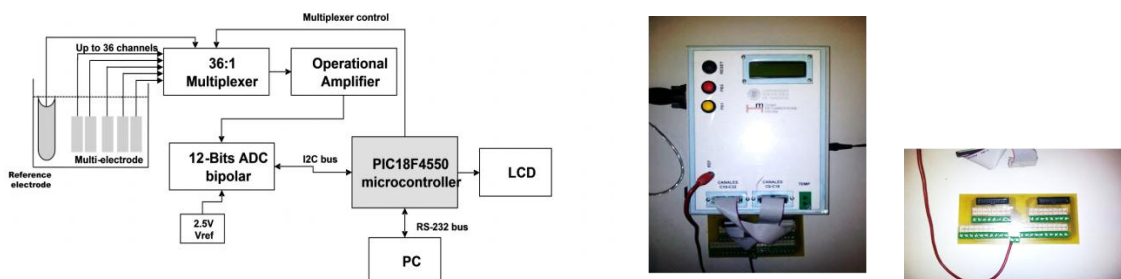Fig. 4 The experimental setup of the electrodes in KCl test solutions

Fig. 5. The block diagram of the measurement system (left) for the data logger (right).

The potentials of the multi-electrodes were acquired using a 36:1 multiplexer architecture, which was formed from two 18:1 channel MOS analogue multiplexers (MAX306, Maxim) and one 2:1 channel analogue multiplexer (MAX308, Maxim). The selection of each channel in the multiplexer was controlled by the microcontroller (PIC18F4550, Microchip Technology). A precision CMOS quad micro power operational amplifier (LMC646, National SMC), was connected to the output multiplexer. This operational amplifier has very high input impedance and an ultra-low input bias current of less than 16fA and hence is suited to the signal impedance generated by the potentiometric multi-electrodes. An analogue to digital converter (MAX128, Maxim) with a resolution of 12-bits was used, with selectable variable external or internal reference voltage in order to obtain different full scale ranges. The software for the PIC18F4550 microcontroller has been designed to scan the voltage for each channel and send the data to a PC via an RS232 serial communications channel. The PC acquisition software was developed using Visual Basic® 6.0 and Microsoft Excel® 2003 software.

3. Results and Discussions

The Thick-Film electrodes were immersed sequentially in different solutions of higher to lower chloride concentration of Sat KCl (A), 1:10 Sat KCl (B), 1:100 Sat KCl (C) and 1:1000 Sat KCl (D) as well as in various pH buffer solutions as shown in Fig. 6 and 7. Their average responses were calculated and plotted. The bare Ag electrode trace most clearly shows the changes in potential between the testing solutions and the duration of the electrodes immersion in each test solution.
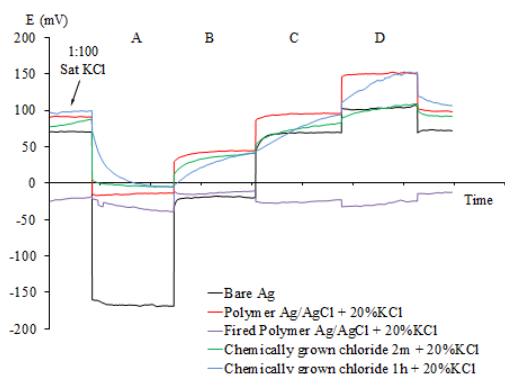

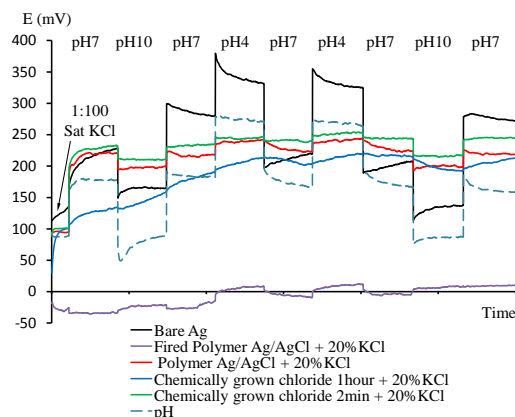Fig. 6. Thick-Film reference electrodes in KCl solutions.

Fig. 7. Thick-Film pH sensors in pH buffer solutions.

To produce a stable voltage from the reference electrode across different ionic concentrations the outer active layers of the electrode consisted of KCl powder in polymer binder to function as a salt matrix layer, which was applied to mimic the commercial gel-filled Ag/AgCl reference electrode design. The grains of the potassium chloride powder form paths in the electrode top layer through which the salt leaches out from the electrode into the electrolyte. Several different concentrations of KCl to polymer binder were tested: 0.6, 3, 6, 20, 66 and 71% by weight respectively. The reference electrodes with the higher concentration of potassium chloride in the salt matrix layer tend to loose salt faster and in consequence their useful lifetime is also more limited. The optimum weight percentage needs to be ratified more precisely, but presently the electrodes with 20% KCl in the outer active layer gave the best results. The Fired Polymer Ag/AgCl + 20% KCl reference electrodes demonstrated nearly stable potential response in all tested solutions in comparison to the Polymer Ag/AgCl + 20% KCl and the two chemically grown chloride electrodes. In all probability, based on the electrode theory, the drift rate of the reference electrodes is also influenced by changes in the AgCl/Ag ratio in the Ag/AgCl paste. It is believed that the optimum ratio of Ag/AgCl still needs to be defined as in all the experiments described here only one type of Ag/AgCl paste was used: Gwent C61003P7, which had an Ag/AgCl ratio of 60:40.

Fig. 8 illustrates the stability of the Thick-Film reference electrodes as a function of chlorine ion concentration. Overall, the performance of the Fired Polymer Ag/AgCl + 20% KCl reference electrode is the most notable in that it gives the flattest and most stable response of all the tested reference electrodes. Table 2 summarises the sensitivities of the various types of Thick-Film reference electrodes. It should be pointed out that the sensitivity of the chemically grown chloride 1 hour electrode was calculated by omitting its apparently anomalous reading in saturated chloride solution.

As previously mentioned and evidenced by Eqn. 3, the potential of the Thick-Film reference electrodes is thought to be influenced by a combination of the chloride ion concentration at the electrode surface and also the ratio of AgCl to Ag forming the electrode surface. Consequently this mechanism may explain the apparently stable behaviour of the Fired Polymer Ag/AgCl + 20% KCl reference electrode. A thin film of sparsely soluble AgCl is believed to form on the surface of the Ag electrode back contact during the process of firing and this has been confirmed through SEM studies of the surface composition of the just fabricated electrode. As the Chloride concentration of the immersion solution decrease the electrode potential will change more positive in line with the Nernst equation. However at the same time the thin layer of sparsely soluble AgCl will be encouraged to dissolve in the lower concentration solution at a higher rate bringing about a reduction in the AgCl/Ag ratio k and hence shifting the electrode potential more negative. Since the AgCl is thin the small changes in its concentration have a pronounced effect on the ratio k at the electrode surface and hence these two mechanisms cancel resulting in the flat response of the electrode to chloride ion concentration change.

Table 2 Chloride ion sensitivity.

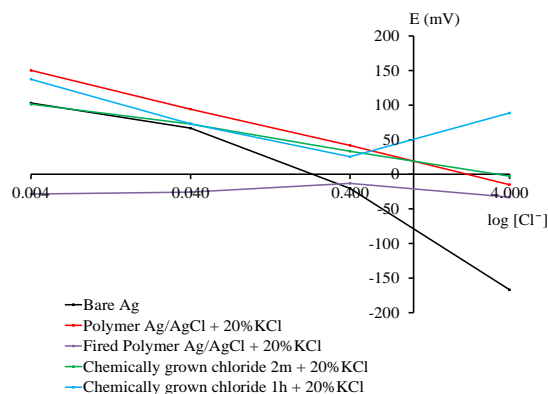| Electrode type	Sensitivity (mV/log Cl⁻)
Bare Ag	-59
Polymer Ag/AgCl + 20%KCl	-30
Fired Polymer Ag/AgCl + 20%KCl	-2
Chemically grown chloride 2min	-20
Chemically grown chloride 1 hour	-30

Fig. 8. Thick-Film reference electrode potentials as a function of chloride ion concentration.

The responses of the different Thick-Film reference electrodes and the Ruthenium Oxide pH electrodes in various pH buffers solutions are shown in Fig. 9. The Ruthenium Oxide pH electrodes show very repeatable and stable response to the pH buffer changes and also reach a stable potential quite rapidly after immersion in the various pH buffers, as can be seen in Fig. 7. Most of the reference electrode potentials exhibited some degree of hysteresis effect when cycled through the pH buffer solutions, possibly through conditioning of the electrodes. However the Fired Polymer Ag/AgCl + 20% KCl reference electrode exhibited a remarkably flat response with very little hysteresis. Table 3 summarises the response in mV/pH of all the Thick-Film electrodes over the range of tested pH solutions.

Table 3 pH sensitivity.

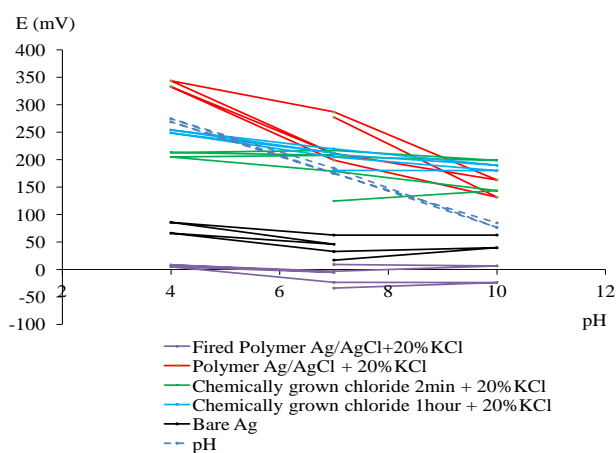| Electrode type	Sensitivity (mV/pH)
Bare Ag	-4
Polymer Ag/AgCl + 20%KCl	-32
Fired Polymer Ag/AgCl + 20%KCl	-2
Chemically grown chloride 2min	-6
Chemically grown chloride 1 hour	-11
pH	-32

Fig. 9. Thick-Film electrode potentials as a function of pH.

The presented results demonstrate the feasibility of the development of low-cost, rugged, miniaturised Thick-Film alternatives to the commercially available liquid electrolyte filled Ag/AgCl reference electrode and glass pH electrode. The results further contribute towards optimisation of the fabrication parameters for screen-printed Ag/AgCl reference electrodes suitable for use in Thick-Film pH sensors.

Acknowledgements

References

[1] Gut U, Vonau W, Zosel J. Recent developments in electrochemical sensor application and technology – a review. *Meas. Sci. Technol.* 2009;**20**:042002

[2] Vonau W, Guth U. pH Monitoring: a review. *J Solid State ELectrochem* 2006;**10**:746-752.

[3] Gac A, Atkinson JK, Zhang Z, Sion RP. A comparison of thick-film chemical sensor characteristics in laboratory and on-line industrial process aplications. *Meas. Sci. Technol* 2002;**13**:2062-2073.

[4] Haskard M, Pitt K. *Thick-Film Technology and Applications*. Port Erin: Electrochemical Publications Ltd; 1997.

[5] Mihell J.A, Atkinson J.K. Planar thick-film pH electrodes based on ruthenium dioxide hydrate. Sensors and Actuators B: Chemical 1998;**48**,1-3: 505-511.

[6] Atkinson J.K, Cranny A.W.J, Glasspool W.V, Mihell J.A. An investigation of the performance characteristics and operational lifetimes of multi-element thick film sensor array used in the determination of water quality parameters. *Sensors and Actuators B: Chemicals* 1999;**54**:215-231.

[7] Atkinson JK, Glanc M, Boltryk P, Sophocleous M, Garcia-Breijo E. An investigation into the effect of fabrication parameter variation on the characteristics of screen-printed thick-film silver/silver chloride reference electrodes. *Microelectronics International* 2011;**28/2**:49-52.

[8] Fog A., Buck R. P. Electronic semiconducting oxides as pH sensors, *Sensors and Actiators* 1984;**5**:137-146.

[9] McMurray H. N., Douglas P., Abbott D. Novel thick-film pH sensors based on ruthenium dioxide-glass composites, *Sensors and Actuators B* 1995;**28**:9-15.