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Performance of miniaturised Thick-Film solid state pH sensors

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Abstract

The performance of novel solid state Thick-Film pH sensor for water quality sampling suitable for deployment in remote catchment areas is described. These miniaturised screen printed planar pH sensors are an alternative to glass pH electrodes, which have many disadvantages such as high-cost, large size, mechanical fragility and limited shape. One of the approaches for improvement of the ruggedness of the pH electrode is the implementation of metal oxides as ion selective electrodes used in combination with screen printed silver/silver chloride (Ag/AgCl) reference electrodes. Various materials of Thick Film pH sensors have been evaluated, these give a sensitivity close to the theoretical Nernstian value of 59mV/pH at 25°C.

Keywords: pH sensor; silver/silver chloride; Thick-Film sensors; water quality

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1. Introduction

Rivers are the habitats for living organisms and any changes of 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 detrimental effects on river health. Agriculture industry is a major user of water resources. It also contributes intensely to water pollution through processes such as use of pesticides, fertilisers, spreading of slurries or manure. To detect the contamination of water courses, a network of early warning systems of in situ water miniaturised electrochemical sensors is required as a simple alternative to the current methods of detecting pollution in rivers [1]. Currently the most widely used technique for determination of pH in the laboratory is the glass type pH electrode. This electrode is a well-established pH sensor because of its

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excellent performances with respect to slop, long-term stability, selectivity, detection limit, and insensitivity versus redox systems [2]. However this traditional glass electrode with an internal liquid reference system exhibits some drawbacks such as mechanical fragility, large size and high cost. Thick-Film technology can resolve these dilemmas by fabricating small, rugged and inexpensive devices which can mimic the commercially available pH electrode and reference electrode [3, 4]. Moreover it can implement a competitive solution to the current expensive environmental monitoring of pH devices by manufacturing sensors in Thick-Film process where metal oxides can be implemented as the pH active layer [2, 6]. In this paper an investigation, formulation and production process of the alternative thick film pH sensors are described. Those devices were fabricated for water catchment area monitoring during routine sample collection to 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 and in order to validate them for environmental sampling further investigations in field trials are required.

2. Fabrication of pH sensors

Thick Film pH sensors consist of two separate electrodes, the pH ion selective electrode and a Ag/AgCl reference electrode. They are attempting to mimic the construction of the conventional glass pH electrode and the single junction electrolyte-filled Ag/AgCl reference electrode [5]. The devices were screen printed onto 96% alumina substrates (Coorstech) by successive layer deposition. The details of the component materials have been documented previously [7]. The devices used in the experimental setup and their basic structures are shown in figure1. The reference electrodes vary in terms of electrode active layer construction (Table 1).

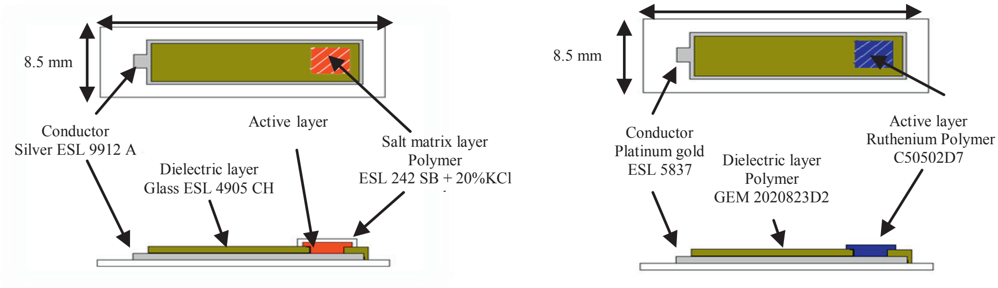

Fig. 1. Cross-sections of Thick-Film reference electrode (left) and pH ion selective electrode (right)

Table 1. Details of the reference electrodes active layer materials.

Electrode type	Polymer Ag/AgCl	Fired Polymer Ag/AgCl	Chemically grown layer 2 m	Chemically grown layer 1h
Active layer	GEM C61003P7	GEM C61003P7	*	*

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

The same polymer bound Ag/AgCl layer (GEM C61003P7) was use for two types of reference electrodes. The Fired Polymer Ag/AgCl electrodes were passed twice through the 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 Ag conductor. Two further types of T-F reference electrodes do not possess the Ag/AgCl layer but a thin layer of AgCl that was chemically grown on the Ag conductor.

The whole experiment was divided in two parts. Firstly the performance of T-F reference electrodes was sequentially tested in different strength KCl solutions, after that a group of the same type of reference electrodes was simultaneously examined with T-F pH electrode in three pH buffers 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 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). T-F sensors were initially hydrated in 1:100 Sat KCl solution overnight and subsequently circled through test solutions (Fig. 2, 3). The electrode potentials were measured with respect to a commercial gel-filled reference electrode (Beckman Coulter A57193). The electrodes were connected through the wired to the voltmeter and the experimental data was recorded in 5 seconds intervals with an own design portable data logger.

3. Results and Discussions

The T-F electrodes were immersed sequentially in different testing solutions (Fig. 2 and 3). The Bare Ag electrode clearly shows the electrodes change between the testing solutions and the electrodes soaking time.

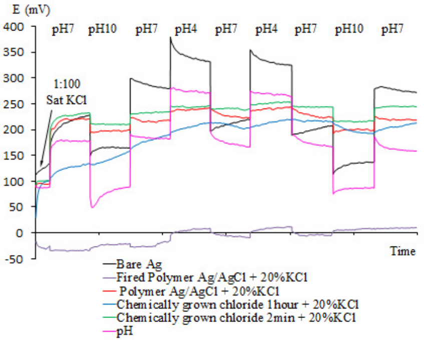

Fig. 2. Thick-Film pH sensors in pH buffers.

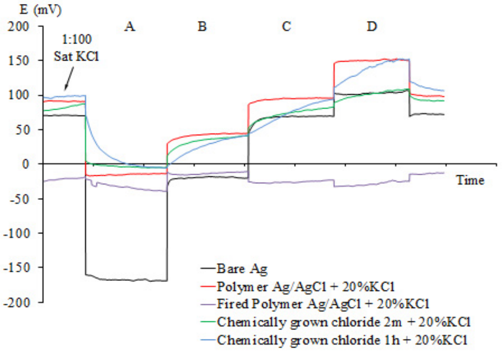

Fig. 3. Thick-film reference electrodes in KCl solutions.

To ensure a stable voltage of 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 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 leach out from the electrode into the electrolyte. Several different weight percentages of KCl with 0.6, 3, 6, 20, 66 and 71% respectively were tested. The reference electrodes with the higher concentration of potassium chloride in the salt matrix layer tend to drift faster and in the consequence their lifetime is also limited. The optimum weight percentage needs to be precisely ratified. Presently the electrodes with 20%KCl in outer active layer give the best results. The Fired Polymer Ag/AgCl + 20%KCl reference electrode demonstrate nearly stable potential response in all tested solutions in comparison to the Polymer Ag/AgCl + 20%KCl and two chemically grown chloride electrodes. Presumably the drift rate of the reference electrodes may also be influenced by the change of AgCl and Ag ratio in the Ag/AgCl paste. The optimum ratio of Ag/AgCl ratio needs to be experimentally defined during further investigations because up to now in all experiments only one type of Ag/AgCl paste was used: Gwent C61003P7 – Ag/AgCl 60:40.

Figures 4 and 5 illustrate the sensitivity of T-F devices to pH and chlorine ion concentration. Overall, the performance of the Fired Polymer Ag/AgCl + 20%KCl reference electrode is noticeable.

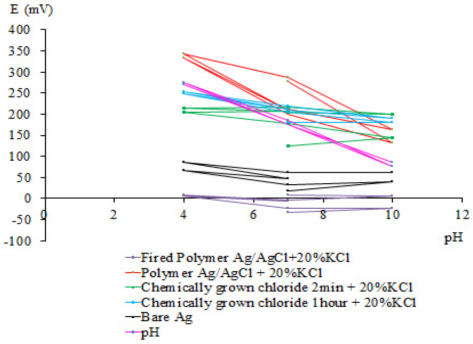

Fig. 4. pH response of T-F pH sensors.

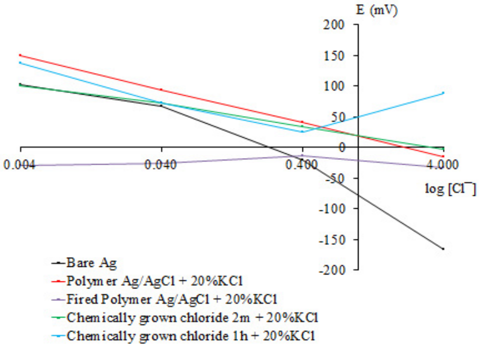

Fig. 5. Chloride ion response of T-F reference electrodes.

Table 2. Sensitivity characteristic of pH sensors

Electrode type	Sensitivity (mV/pH)	Sensitivity (mV/log Cl¯)
Bare Ag	-4	-59
Polymer Ag/AgCl + 20%KCl	-32	-30
Fired Polymer Ag/AgCl + 20 %KCl	-2	-2
Chemically grown chloride 2 min	-6	-20
Chemically grown chloride 1 hour	-11	+0.6
pH	-32	

The responses of T-F references electrodes stand out in higher pH buffers and possibly it is caused by sudden changes in pH while they were circled through different buffer solutions (Fig. 4). The pH electrode show practically stable response to the pH buffer changes and it also has reached stable potential values immediately after immersion in various pH buffers. The presented results contribute towards optimisation of the fabrication parameters of low cost miniaturised screen-printed pH sensor and demonstrate the feasibility of the development of a miniaturised alternative to the commercially available liquid electrolyte filled Ag/AgCl reference electrode and glass pH electrode using Thick-Film technology.

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