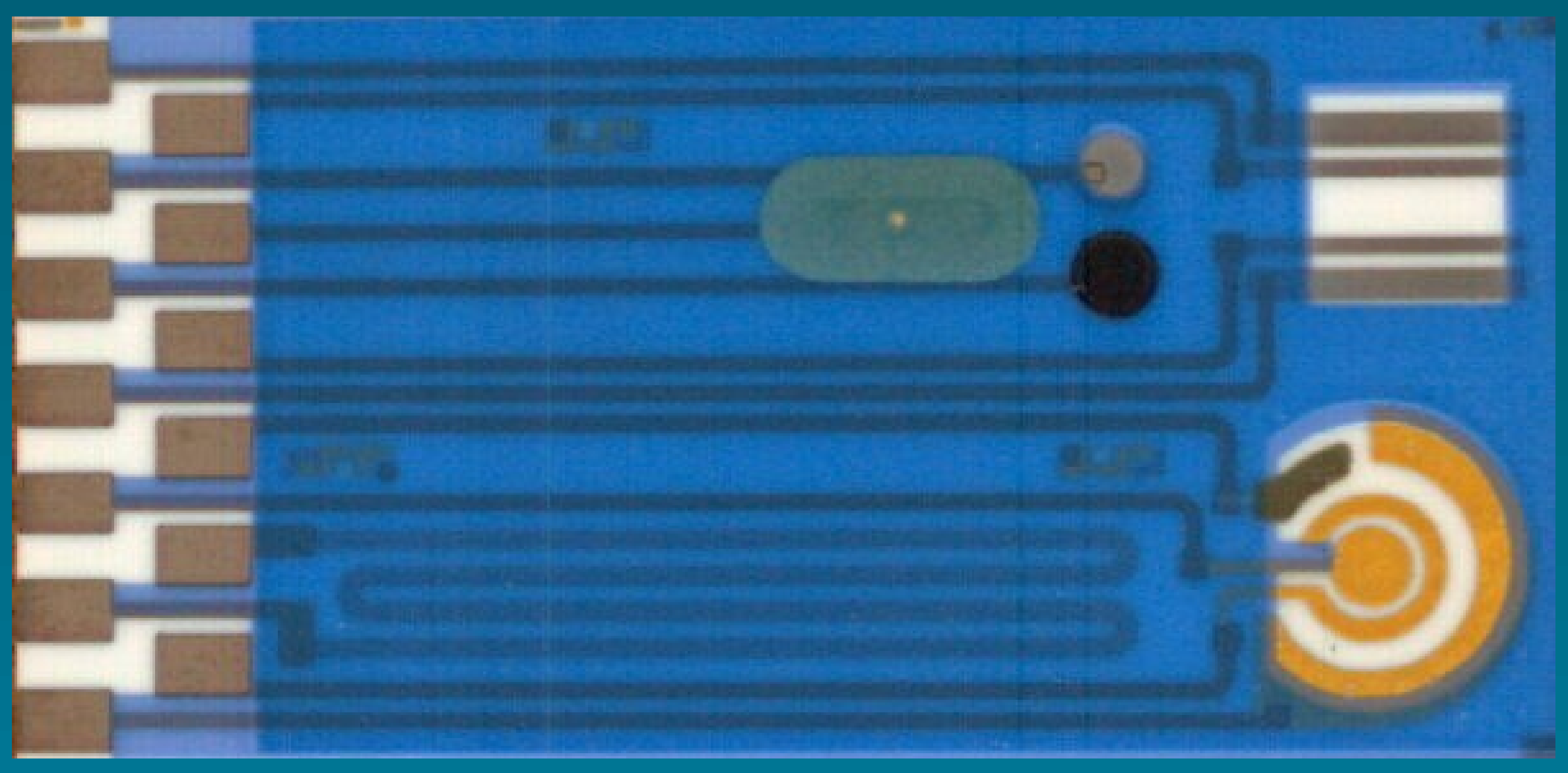

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An investigation into the effect of fabrication parameter variation on the characteristics of screen printed thick film Ag/AgCl reference electrodes

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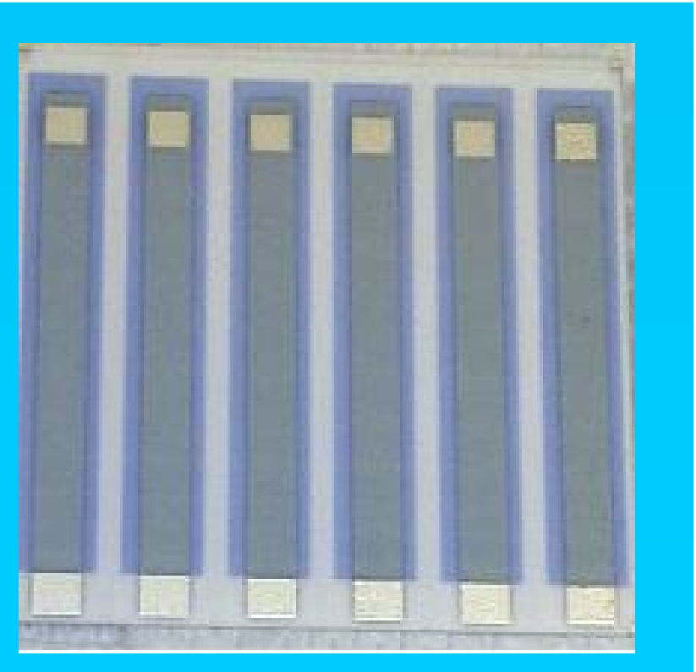
Abstract

Fabrication parameters of screen printed thick film reference electrodes have been experimentally varied and their effects on device characteristics have been investigated. The tested devices were fabricated as screen-printed planar structures consisting of a silver back contact, a silver/silver chloride interfacial layer and a final salt reservoir layer containing potassium chloride.

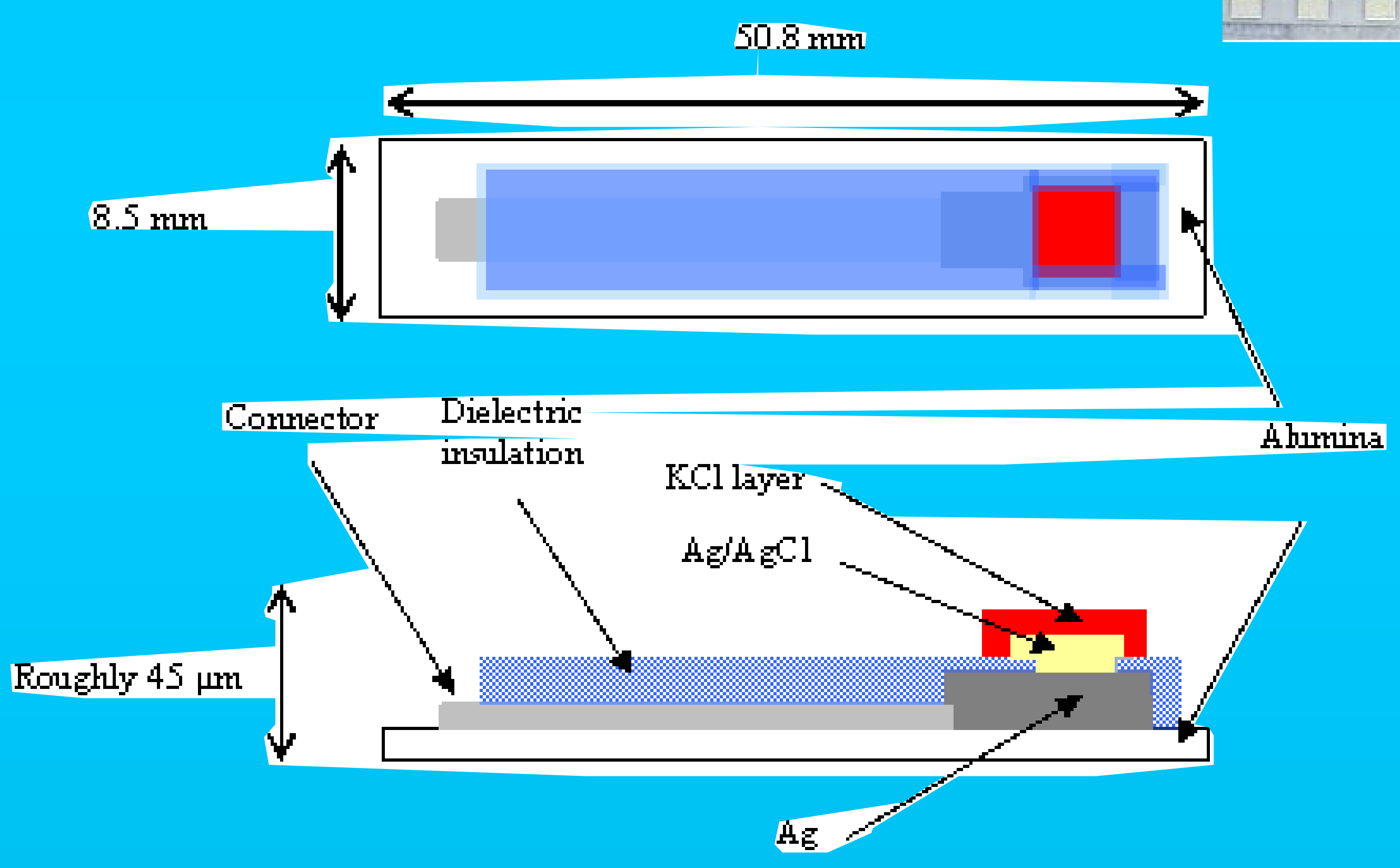
Introduction

The reference electrodes reported here were designed to give some measure of electro-potential stability in a similar manner to that of a conventional electrolyte filled reference electrode. Earlier attempts at fabricating such devices concentrated on the use of a polymer bound salt matrix (KCl) layer that was screen printed onto a screen printed Ag/AgCl layer. These devices have been employed successfully on chemical and environmental arrays for use in a range of application areas (see example photo top left of this poster showing a thick film sensor array for the simultaneous monitoring of conductivity, pH, temperature, dissolved oxygen and oxygen reduction potential). The results reported here are for devices where the initial KCl concentration in the salt matrix is varied.

Electrode Fabrication

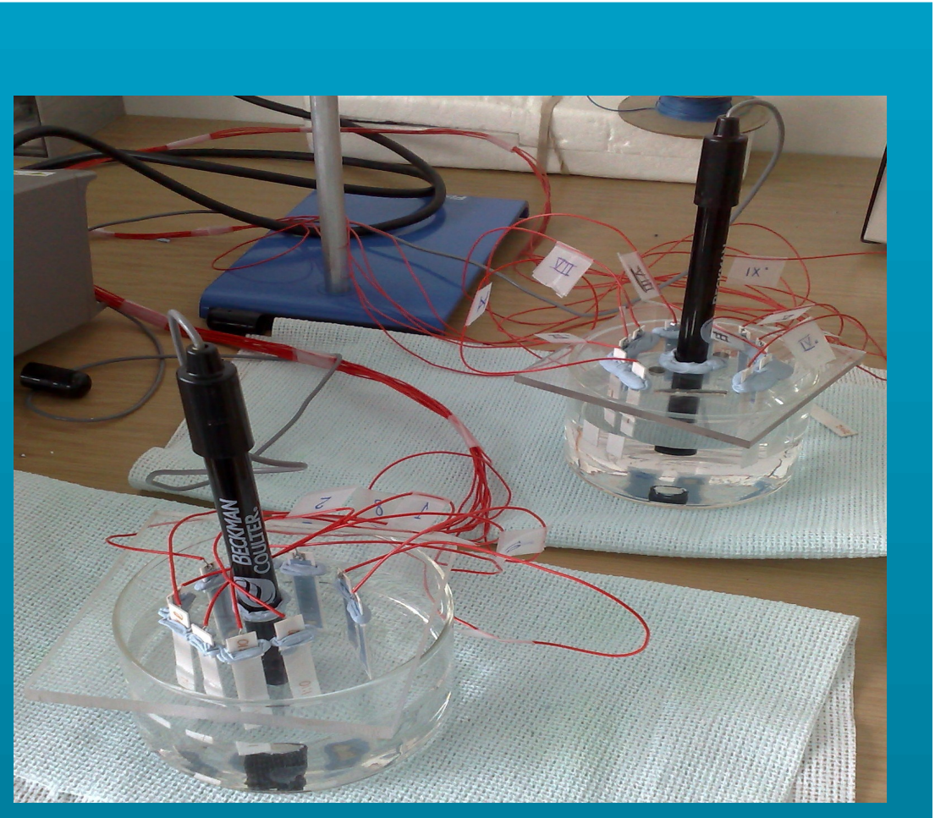


For convenience the test electrodes were fabricated on 50.8 mm square, 0.625 mm thick 96% alumina substrates (Coorstech) prescribed with laser lines to produce substrates that could be used for the simultaneous fabrication of 6 electrodes at a time (see photograph right). Individual electrodes could then be snapped from the substrate along the laser scribes.



The cross-sectional view of the individual reference electrodes shown above reveals the construction as a succession of screen printed layers commencing with a silver conductor layer (ESL 9912) onto which is deposited an insulating glass layer (ESL 4905) with a 5mm x 5mm window that exposes the underlying silver layer. A layer of glass bound silver/silver chloride paste (GEM C61003P7) is then printed and fired on top of the silver exposed in the window before a second layer of insulating glass with the same 5mm x 5mm window opening as before is deposited on top. Finally a layer containing potassium chloride is deposited onto the silver/silver chloride layer. Two different types of KCl layer were tested, one consisting of a silicone based polymer paste (ESL 242SB) containing different concentrations of potassium chloride of approx 6%, 3% and 0.6% by weight and the other a solgel made from commercially obtained gelatine dissolved in different concentrations of KCl solution (saturated, saturated diluted with deionised water in ratios of 1:2 and 1:10). The polymer bound salt reservoir was screen printed onto the Ag/AgCl electrodes while the solgel solutions were applied by a dropper to give an approximate droplet volume of 3 ml per electrode.

Testing

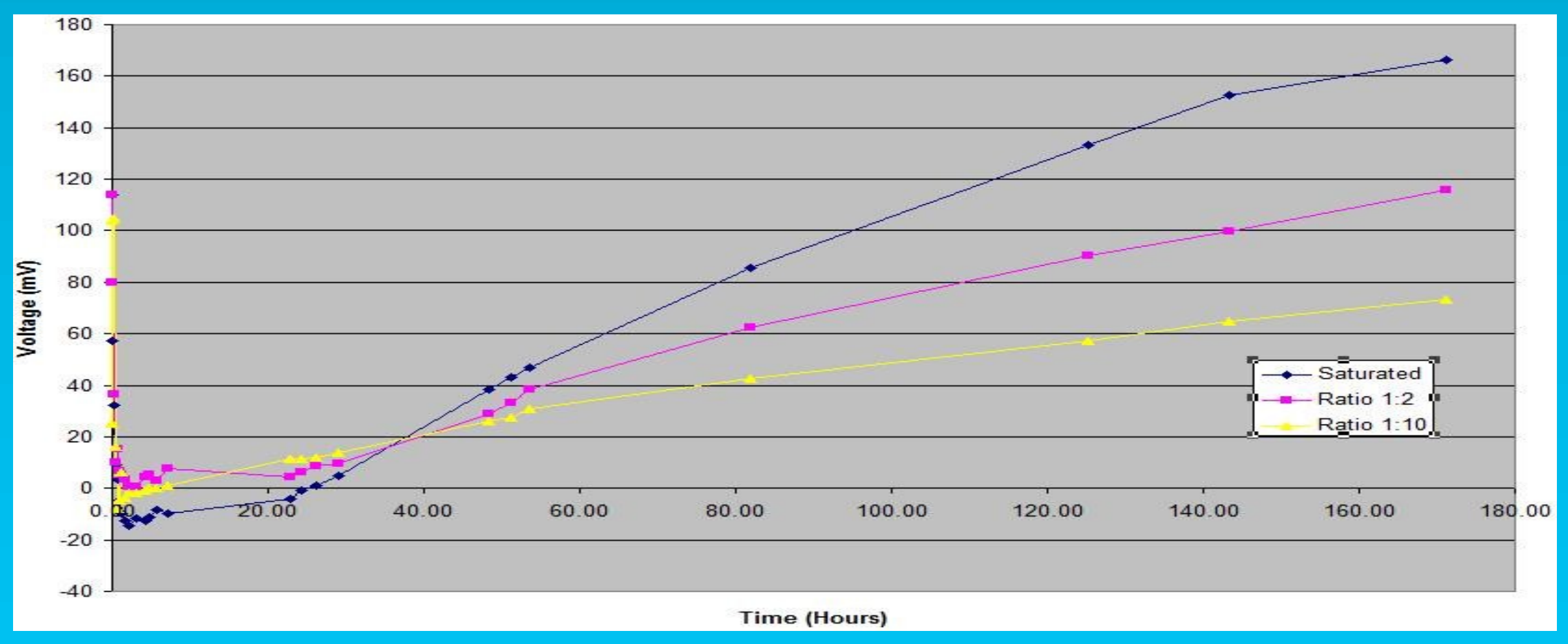


The individual reference electrodes were initially hydrated in dibasic sodium phosphate/monobasic potassium phosphate pH7 buffer solution (Oakton) and their electrode potentials measured with respect to a commercial double junction reference electrode (Beckman Coulter A57193) using a Keithley 2000 digital multimeter. The electrodes were connected to the multimeter in batches of 10 at a time using a K2000 scan card and held in solution using the mounting plate arrangement illustrated in the photograph right.

Different concentrations of potassium chloride test solutions were made by first of all dissolving potassium chloride (BDH 101984L AnalaR) in deionised water until saturation and then diluting this solution with deionised water in subsequent ratios of 10 to 1, designated SAT, SAT 1:10, SAT 1:100 and SAT 1:1000. The electrodes were then immersed in each test solution and allowed to stabilise for approx one hour before their individual potentials versus the commercial reference electrode were recorded.

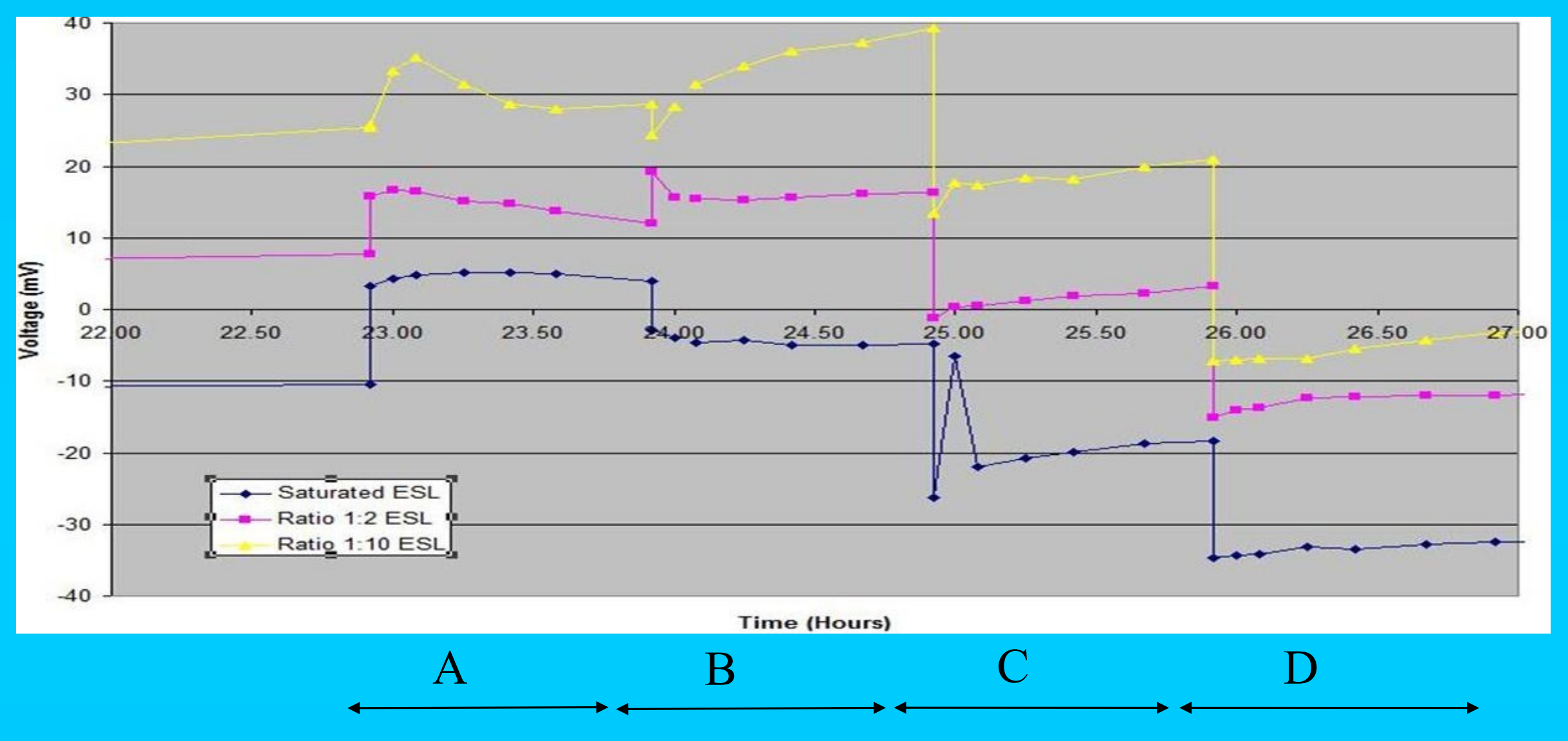
Results

ESL 242-SB/KCl electrodes hydrating and then drifting in pH 7 buffer



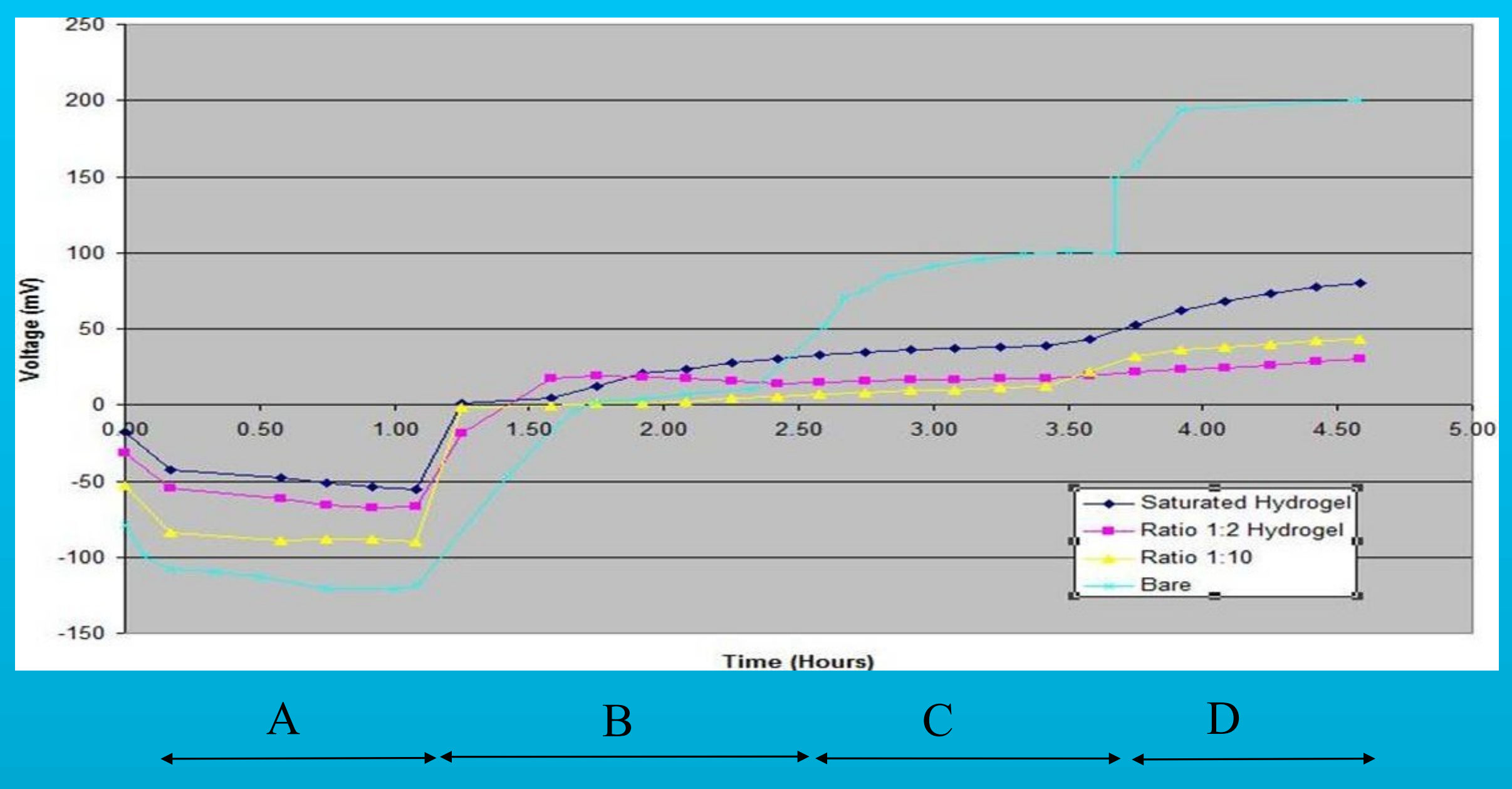
After an initial period of electropotential instability lasting approx one hour the electrodes hydrate and remain relatively stable for a period of approximately 24 hours. After this period they begin to drift at different rates. It can be seen that the higher the initial concentration of potassium chloride contained in the electrodes the faster they drift.

ESL 242-SB/KCl electrode potentials in different concentration KCl solutions



Successive immersions in solutions of deionised water containing KCl concentrations of A: SAT, B: SAT 1:10, C: SAT 1:100 and D: SAT 1:1000 produced potential steps of approximately 10mV per decade of KCl concentration with the step sizes being noticeably smaller for electrodes containing higher initial concentrations of KCl. It should also be noted that the electrode potentials became more NEGATIVE with DECREASING KCl solution concentration.

Hydrogel/KCl electrode potentials in different concentration KCl solutions



Successive immersions of the hydrogel electrodes in solutions of deionised water containing the same KCl concentrations as before showed large potential steps for each electrode type when moving from SAT to SAT 1:10 but much lower potential steps thereafter when moving between lower solution concentrations. A bare Ag/AgCl electrode is shown on the same graph for comparison and exhibits step sizes of approx 100mV per decade change in KCl solution concentration. It should be noted that for the hydrogel electrodes the electrode potentials became more POSITIVE with DECREASING KCl solution concentration.

Conclusions

The reason that the ESL242SB/KCl electrodes gave a potential response to different concentrations of chloride solution that was the **opposite** of the both the bare Ag/AgCl and the solgel electrodes is thought to be due to a combined response of the silicone polymer itself and the KCl salt concentration in the polymer. The fact that higher concentrations of KCl gave lower step sizes would tend to suggest that increasing the KCl concentration to an optimum level will result in electrodes that have responses to varying chloride concentration that are almost flat, whereby the KCl response “cancels out“ the silicone polymer response. Conversely, the drift rates of the hydrated ESL242SB/KCl electrodes were heavily influenced by their initial salt concentrations, which is thought to be a function of the number of “pathways” through which the salt can leach out of the polymer binder. This tends to suggest that higher initial KCl levels would result in shorter useful lifetimes as a result of higher drift. The solgel electrodes appear to offer some promise in that they hydrated far more rapidly (within minutes) and hence gave a useful lifetime sooner than their polymer counterparts. One possibility would be to combine these characteristics in a device whereby the polymer electrode surface is covered with a solgel membrane to reduce salt leach out rates.

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