

Figure 1: An example of in-field application of required sensor arrays^[1]

Environmental scientists have been trying to understand the complex mechanisms of nature and more precisely those relating to rivers and floodplains [1, 2]. Reliable and thorough investigations of rivers or floodplains require a dense array of chemical sensors without an attendant high cost. Thick-Film technology features low production cost and the ability to produce multiple rugged, robust and miniaturized sensors on the same substrate [3].

Electrochemical, potentiometric cells consisting of a reference and an ion selective electrode (ISE) have been used but problems mainly arise from the reference electrodes, while the ISE's can provide reliable results.

Reference electrodes are required to maintain a stable potential.

Commercial reference electrodes are bulky, fragile and expensive.

In need of reliable, solid-state, non-disposable reference electrodes.

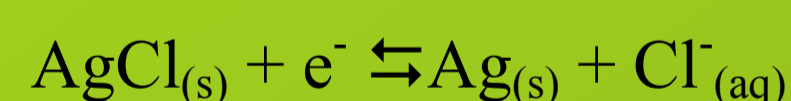


Figure 2: A commercial silver/silver chloride (Ag/AgCl) reference electrode (left), Thick-Film electrode (right).

Electrode Operation

The potential difference between the two electrodes is measured and any change in that potential corresponds to a change in the concentration of the investigated species. ISE's respond to the concentration changes while reference electrodes are ideally expected to maintain a stable and constant potential in any solution that they are immersed.

Ag/AgCl reference electrodes undergo the reversible reaction shown below [4, 5]:



The potential of such an electrode is calculated using the Nernst equation [4,5]:

$$E = E^0 + (RT/nF) \ln(\alpha_{\text{AgCl}} / (\alpha_{\text{Ag}^+} \alpha_{\text{Cl}^-}))$$

Activity of a species (α) is defined as the product between the activity coefficient and the concentration of the species.

AgCl is a sparingly soluble salt and it immediately saturates the solution maintaining a stable activity. Ag^+ on the other hand, is dependent on the activity solubility product which is invariant at a given temperature.

Activity solubility product is defined as the product between the activity of Ag^+ and Cl^- in the solution.

If the surrounding chloride activity is constant the electrode will maintain a stable potential.

Activity coefficient for moderate Cl^- solutions is close to 1, therefore, the activity can be substituted by concentration [5, 6].

Electrode Fabrication & Testing

Electrodes are designed to mimic their macro-scale equivalent therefore, the structure of the different investigated types is similar.

The electrodes are Screen-Printed using one screen for each layer.

Stainless steel screens with 250 lines per inch and 45° mesh were used for all the layer except the ones containing the salt matrix. Those were polymer 70W PW 123-70W:133µm mesh-opening with emulsion photopolymer POLYCOL UNO: 113µm thickness.

The different inks used for each layer are shown in table 1:

Table 1: Inks used

Layer	Silver Conductor	Dielectric layer	Ag/AgCl	Salt Matrix
Ink	ESL-9912-A	ESL 4905-C	PPCFB2 PPCFB3 GEM C61003P7	ESL 242-SB

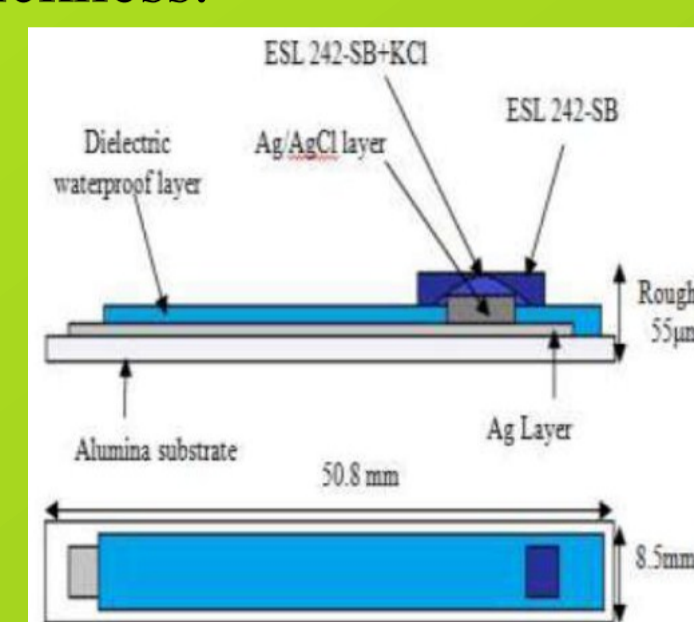


Figure 3: A schematic of the electrode's structure

Results

Test 1 involved various different Ag/AgCl pastes with the same upper KCl containing layers.

The average over about one hour was calculated for each chloride concentration and graphs were plotted on a logarithmic scale (Figure 5).

Electrode susceptibility decreased when the printed Ag/AgCl layer was omitted leaving a bare Ag electrode.

A thin layer of AgCl is formed on the Ag electrode after the deposition of the KCl salt matrix layer. The Ag/AgCl ratio in this thin layer can more easily be changed due to the chloride ion concentration.

Test 2 (Figure 5) was performed on electrodes without the Ag/AgCl layer with overlaid polymer salt matrices of various KCl content by weight. A further layer was deposited on top of these containing either ESL242-SB with no added KCl or 20% KCl by weight.

Table 2: List of electrode types and their susceptibilities

No	Type	Susceptibility (mV/decade change in chloride concentration)
1	Ag+ESL 242-SB 20% KCl+ESL 242-SB	2
2	Ag+ESL 242-SB 20% KCl+ESL 242-SB 20% KCl	2
3	Ag+ESL 242-SB 50% KCl+ESL 242-SB	2
4	Ag+ESL 242-SB 50% KCl+ESL 242-SB 20% KCl	4
5	Ag+ESL 242-SB 66% KCl+ESL 242-SB	-35
6	Ag+ESL 242-SB 66% KCl+ESL 242-SB 20% KCl	-9
7	Ag+ESL 242-SB+20%KCl	11
8	Ag+PPCFB2+ESL 242-SB+20%KCl	-43
9	Ag+PPCFB3+ESL 242-SB+20%KCl	-29
10	Ag+C61003P7+ESL 242-SB+20%KCl	-81

Drift tests were carried out in two experiments in approximately 0.04 M KCl solution for about 10,000 minutes and about 6,500 minutes respectively (Figure 7).

The electrodes undergo a reversible reaction when immersed and the equilibrium state is established in a relatively short time. Electrodes having KCl in the upper layer established equilibrium faster with a lower drift.

The electrodes with no KCl on the upper layer initially maintained a stable potential at a value established by the KCl concentration of the lower layer, but after approx. 3 days they converged to the same potential as the rest of the electrodes.

Above a certain amount of KCl, the adhesion of the paste decreases and there is a more rapid leakage of KCl, increasing the susceptibility to the surrounding solution.

Conclusions & Further Work

The performance of the electrodes was optimized at a susceptibility level of 2 mV/decade chloride ion concentration change.

Longer term drift is still a major drawback for this design.

While a sufficient KCl level is maintained in the electrodes they perform very well, but once the KCl is dissolved in the solution the electrode drifts to a different potential depending on the concentration of the immersed solution.

Future experiments are designed to find a way of holding the salt matrix on the electrode longer by the use of different pastes or membranes.

The electrodes were tested against a commercial liquid filled Ag/AgCl reference electrode.

The solutions were made by dissolution of KCl (BDH 101984L AnalaR) in distilled water. Solutions were continuously stirred using a magnetic stirrer to minimize any mass transport effects.

For the susceptibility experiments, the electrodes were placed in solution of approximately 0.04 M overnight for approximately 14 hours and then placed in varying KCl concentration solutions of between 4M and 0.004M and left for about an hour in each solution.

After every solution, the electrodes were washed in distilled water to remove any surface depositions of KCl from the electrodes.

Susceptibility readings were recorded automatically while drift test data were manually acquired.



Figure 4: Experimental Setup

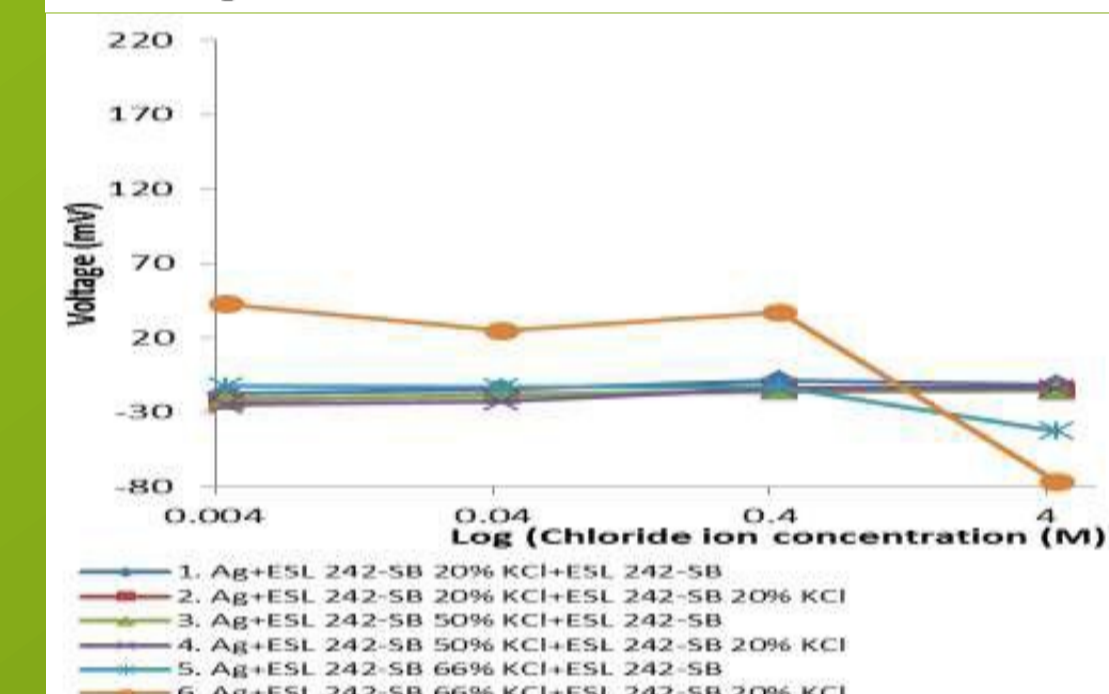
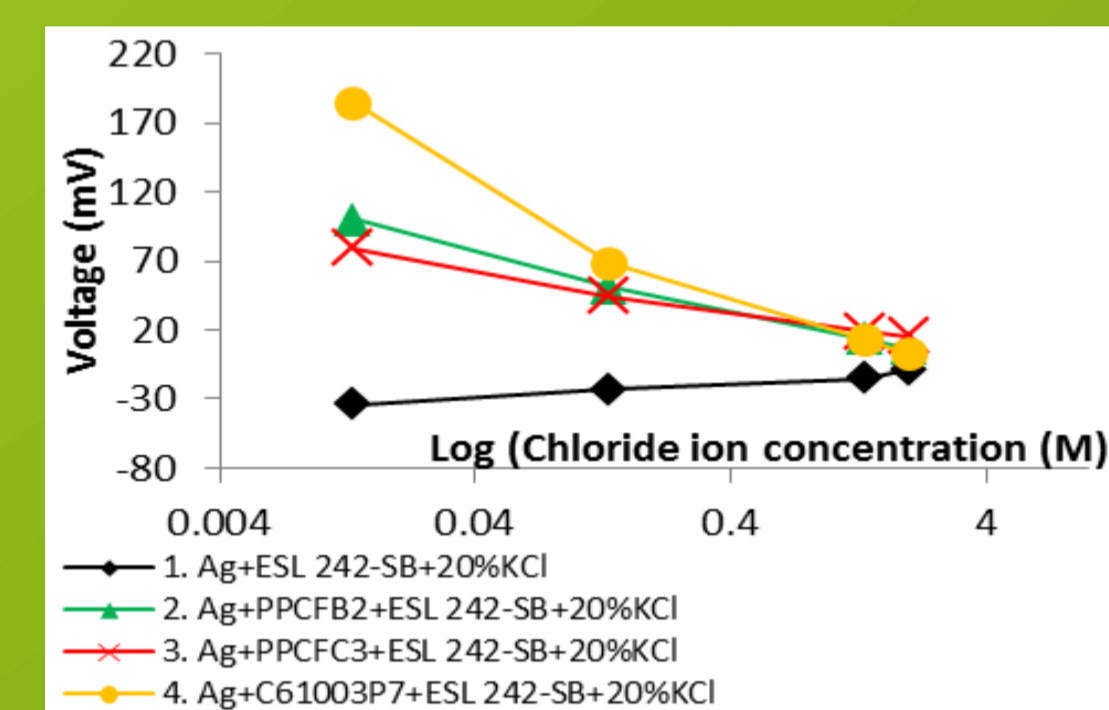


Figure 5: Voltage versus chloride concentration Test 1 (upper), Test 2 (Lower)

Susceptibilities were significantly reduced using the extra top layer.

The lower the amount of KCl and therefore the lower the porosity of the layer, the smaller the susceptibility on the concentration variations.

The lower the amount of KCl in the underlying layer, the lower the conductivity of the electrodes increasing their susceptibility to noise.

The more KCl, the less the adhesiveness of the paste causing the salt matrix to dissolve more rapidly in the solution. The complete list of the investigated types and their susceptibility is shown on Table 2.

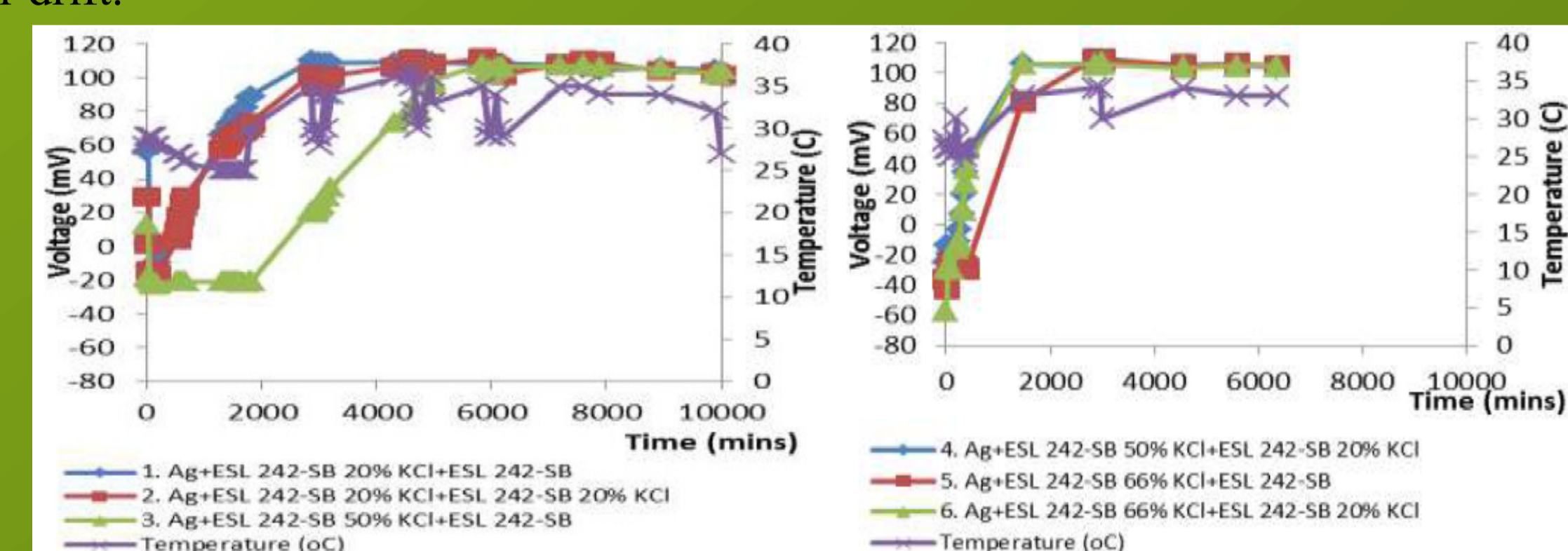


Figure 7: Voltage versus time for the drift experiments, Experiment 1 (Left), Experiment 2 (Right)

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Corresponding author:

Marios Sophocleous, Faculty of Engineering and the Environment, University of Southampton, SO17 1BJ, United Kingdom

Email:ms3e11@soton.ac.uk