An Experimental Analysis of Thick-Film Solid-State Reference Electrodes

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***Abstract*— Thick-Film planar solid-state Silver/Silver Chloride (Ag/AgCl) reference electrodes were developed and tested for ion susceptibility and long term drift in approximately 0.04 M potassium chloride (KCl) solution. Various types of electrodes were tested exhibiting stabilities down to 2 millivolts per decade change of chloride concentration. It is demonstrated that Thick-Film reference electrodes are suitable for use in underground soil measurements due to their ruggedness and robustness.**

I. INTRODUCTION

Determination of soil and water quality is nowadays receiving quite a high level interest. Environmental scientists have been trying to understand the complex mechanisms of nature and more precisely those relating to rivers and floodplains[1]. Protection agencies are interested in on-line monitoring of river water quality[2] for a deeper understanding of aquatic life dependence on various parameters. On-line chemical analysis of specific species in water has been applied previously[3] but with some serious drawbacks.

Electrochemical 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[4]. Most laboratory equipment used for chemical analysis is based on silver/silver chloride (Ag/AgCl) reference electrodes which are made up of a liquid-filled tube[5] making the electrode fragile and inappropriate for use underground and outside of the laboratory environment. Attempts at solid-state Ag/AgCl reference electrodes have been reported[5-12] employing various techniques appropriate for the specific application of the electrode.

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[13]. Early attempts at Thick-Film Ag/AgCl reference electrodes have been reported[11] with promising results, while some more recent efforts have provided an enhanced performance for such electrodes[4].

The lack of all-solid-state Ag/AgCl reference electrodes, especially non-disposable, has been a main drawback for lab-on-a-chip type chemical sensors. Screen printed Thick-Film reference electrodes can be an innovating alternative to the classic liquid-filled electrodes and allow for easier lab-on-a-chip integration. Screen printed Thick-Film Ag/AgCl reference electrodes, mimicking their macro-scale equivalents, were fabricated and their performance was thoroughly investigated as an initial step towards a deeper understanding of the operating mechanisms involved. Deeper knowledge of the electrode's operation can provide the opportunity for better optimization of the performance of the electrodes.

A. *Background Theory*

Simplest electrochemical cells used for chemical analysis often employ potentiometric measurements. The potential difference between the two electrodes is measured and any change in that potential corresponds to a change of the investigating species' concentration. 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:

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

while the potential of such an electrode is calculated using the Nernst equation:

$$E = E^{\theta} + (RT/nF)\ \ln(\alpha_{AgCl}/(\alpha_{Ag^{+}})(\alpha_{Cl^{-}})) \qquad (2)$$

Commercial liquid-filled electrodes have a stable potential which is in fact only dependent on the chloride activity. Activity of a species is defined as the product between the activity coefficient and the concentration of the species. In this case, 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. Therefore, if the surrounding chloride activity is constant the electrode will maintain a stable potential. Activity coefficient for moderate Cl^- solutions is close to 1 and therefore, the activity can be substituted by concentration.

II. EXPERIMENTAL DETAILS

A. Fabrication

The investigation was based on variation of material selection for the construction of the reference electrode. Although the basis of most of the materials is the same, concentration variations as well as addition and subtraction of certain layers were applied. The construction of the electrode is designed to mimic the operation of a commercial liquid-filled electrode. A typical construction of a Thick-Film Screen printed Ag/AgCl reference electrode is shown in Figure 1.

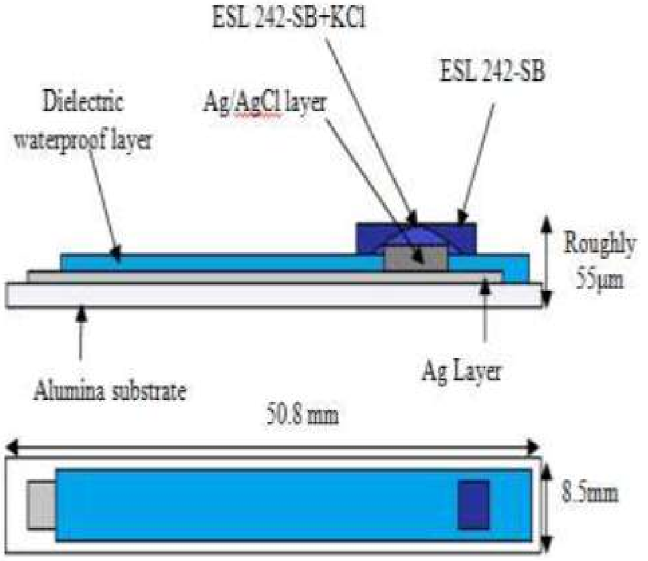

Figure 1: Construction of a typical screen printed Ag/AgCl reference electrode

Screens for each layer were designed using AUTOCAD to ensure precise sizing. Each screen was designed to print a single layer of the electrode. The first layer, silver conductor, was a rectangle with dimensions of 2.25 mm x 44.55 mm. Secondly; a dielectric layer was applied, leaving a small window exposing the underlying conductor. The exposing window was of size 3.4 mm x 3.4 mm. On the other end, silver was exposed as a soldering pad, approximately 4.15 mm x 2.25 mm, as shown in Figure 1. The Ag/AgCl screen was a square window of 4 mm x 4 mm, slightly bigger than the exposed silver to ensure complete coverage of the silver. For the last two layers, the screens had square mesh openings with increasing dimensions of 4.5 mm x 4.5 mm and 5 mm x 5 mm respectively, to ensure complete coverage and proper adhesion of the paste on the electrode.

Screens for the first three layer were stainless steel with 250 lines per inch and 45^o mesh, while the last two were polymer 70W PW 123-70W:133µm mesh-opening with emulsion photopolymer POLYCOL UNO: 113µm thickness.

Commercial pastes were used for most of the active layers of the electrodes. ESL 9912-A was used as a silver conductor, while the dielectric layer was achieved using ESL 4905-C. Ag/AgCl layer was one of the varying parameters so 3 different pastes were used.

The first paste was commercially obtained GEM C61003P7 and two further glass based pasted were developed. PPCFC3 was made of AgCl (Aldrich 227927) milled to 400 rpm/30min with ethanol (Pulverisette Fritsch), sieve/100µm, Ag (Aldrich 32708-5) sieve/100µm, powder frit (Ferro CF7567FC) sieve/100µm, vehicle (Heraeus V-006), mixed in the ratios 3gr Ag + 3gr AgCl + 2gr frit + 3.84gr vehicle and triple roll milled for 5 minutes. PPCFB2 was developed similarly with the only difference being the powder frit (Ferro EG2020VEG).

On top of the Ag/AgCl layer a commercial polymer based ink (ESL 242-SB) was used which also included varying amounts of KCl. All commercial pastes were dried and cured at the prescribed temperatures and times specified by the manufacturers. The two glass-based Ag/AgCl pastes were fired at 390 and 420 respectively in a 4 zone belt furnace.

B. Experimental Setup

The electrodes were tested against a commercial liquid filled Ag/AgCl reference electrode (Beckman Coulter). The electrodes were soldered on wires connected on a voltmeter provided by the Universidad de Valencia while the drift tests were performed using a multimeter (Keithley 2000). The electrodes were mounted on a planar slotted disk as shown in Figure 2 for proper immersion in the testing solution.

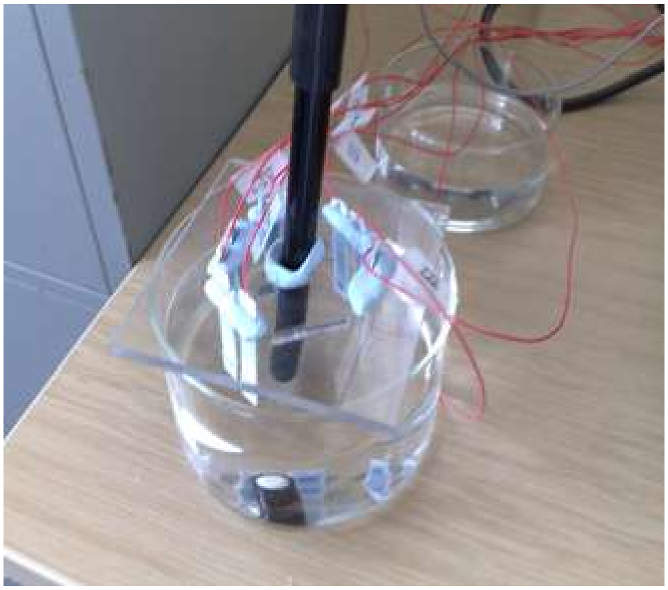

Figure 2: Experimental electrode configuration

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. Readings were recorded automatically using the voltmeter from Valencia University and were automatically imported into a spread sheet for easier and more accurate data acquisition. Drift test data were manually acquired from a Keithley 2000 voltmeter.

III. RESULTS AND DISCUSSION

Initial experiments (Test 1) involved various different Ag/AgCl pastes underneath the same upper polymer bound salt matrix layer of 20% KCl by weight. The average of the acquired readings over approx. one hour was calculated for each chloride concentration and graphs were plotted on a logarithmic scale in order to better compare their slopes with the theoretical values. Results of electrode potential versus chloride concentration are shown in Figure 3.

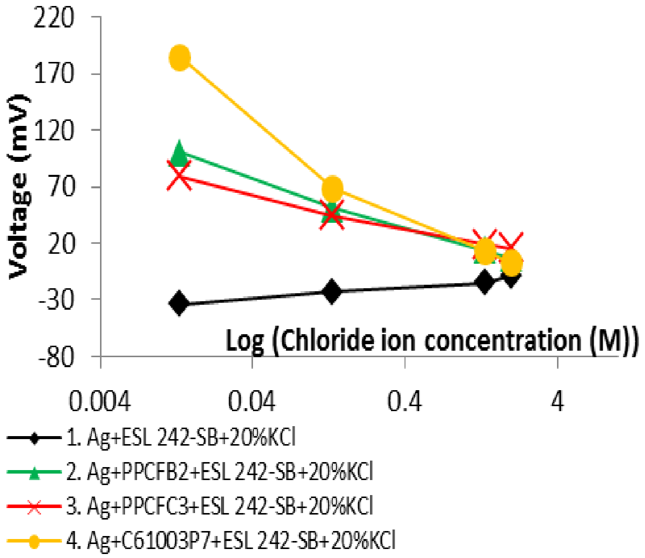

Figure 3: Susceptibility Test 1,Voltage vs Chloride ion concentration

It was observed that the susceptibility of the electrodes decreased if the Ag/AgCl layer was not present and this is thought to be due to changes in the Ag to AgCl ratio affecting the potential of the electrode in a manner contrary to the chloride ion response. Even without added AgCl, a thin layer of AgCl is formed on the Ag electrode during the fabrication process and more specifically 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. Based on that observation, more experiments were carried out (Test 2) on electrodes without the Ag/AgCl layer and 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. These various combinations are detailed in Table 1.

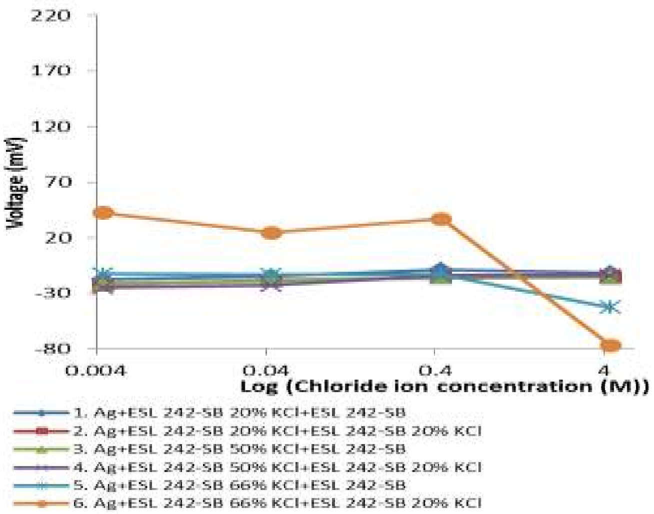

Figure 4: Susceptibility Test 2, Voltage vs Chloride ion concentration

Susceptibility of the electrode was significantly reduced using the extra top layer. Most probably the porosity of the layer depends on the amount of KCl present in the upper layer and consequently the electrodes without any KCl in the upper layer tend to be less affected by the concentration changes. There is a trade-off concerning the amount of KCl in the underlying layer. A smaller amount of KCl decreases the conductivity of the electrodes increasing their susceptibility to noise. On the other hand, higher amounts of KCl can decrease the adhesiveness of the paste causing the salt matrix to dissolve very fast in the solution. The various susceptibilities are shown in Table 1 below.

TABLE I. ELECTRODE 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+ES2 L 42-SB+20%KCl*	*-43*
9	*Ag+PPCFC3+ESL 242-SB+20%KCl*	*-29*
10	*Ag+C61003P7+ESL 242-SB+20%KCl*	*-81*

Drift tests were also performed on the electrodes with the double overlayer. The drift tests were carried out in two different experiments due to a shortage of channels on the

Keithley 2000 voltmeter. The electrodes were placed in approximately 0.04 M KCl solution and the voltage was recorded for about 10,000 minutes for the first experiment and about 6,500 minutes for the second. Results are shown in Figure 5 and 6 as well as the temperature variations.

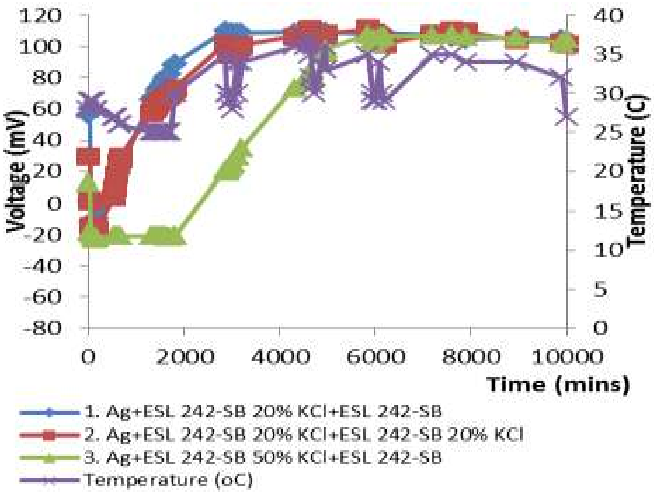

Figure 5: Drift Test 1, Voltage vs Time

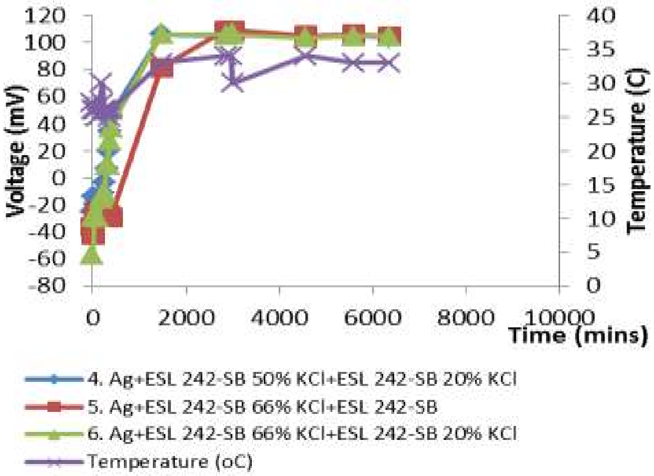

Figure 6: Drift Test 2, Voltage vs Time

The drift tests showed that when the electrodes are immersed in the solution they undergo a reversible reaction and the equilibrium state is established in a relatively short time. The electrodes having KCl in the upper layer established equilibrium faster and did not drift significantly. 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.

In this case, there is also a trade-off between the percentage of KCl in the underlying layer, since above a certain amount the adhesion of the paste decreases and cannot hold the salt matrix on the electrode allowing for more rapid leakage of KCl into the solution and increased susceptibility to the surrounding solution, as can be seen in Figures 5 and 6.

IV. CONCLUSION

Following investigation of the Ag/AgCl reference electrodes, the performance was optimized at a susceptibility level of 2 mV/decade chloride ion concentration change, although the electrodes suffered from a more rapid KCl leakage changing the structure and performance of the electrodes. As such the susceptibility of the optimized electrodes is significantly improved for any given application, although longer term drift is still a major drawback for this design. While a sufficient KCl level is maintained in the electrode 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.

ACKNOWLEDGMENT *(HEADING 5)*

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