A review of screen-printed silver/silver chloride (Ag/AgCl) reference electrodes potentially suitable for environmental potentiometric sensors

Marios Sophocleous [1,*], John K. Atkinson [2]

[1]Holistic Electronics Research Lab, Department of Electrical and Computer Engineering, University of Cyprus, Nicosia, Cyprus
[2]Faculty of Engineering & the Environment, University of Southampton, Southampton, UK

Abstract: The screen-printed (SP), reference electrode (RE) has been shown to be a crucial element of potentiometric sensors but it is also the stumbling block for reliable and accurate SP sensors. The easiest, most common and most environmentally friendly, type of RE is the Silver/Silver Chloride (Ag/AgCl) RE. Unfortunately, until now the only reliable RE of this kind is the conventional, liquid or gel-filled type. However, for most environmental and soil applications the use of the conventional RE is not an option, which raises the demand for a robust, rugged and low-cost version to replace the conventional RE. This paper presents a review of the various attempts to produce reliable, SP, Ag/AgCl REs, and explain why almost all of them never reach the commercialisation stage. The paper provides an overview of the main challenges that need to be overcome, details of the electrode's construction, an analytical comparison of their performance in terms of chloride susceptibility, cross-sensitivity and lifetime, and their suitability in different applications depending on their performance characteristics.

Keywords: Screen-printing, Reference electrodes, Silver/silver chloride, Ag/AgCl, Thick-Film, Solid-state.

1. Introduction

The continuous increase in legislation concerning health and safety, food and soil quality, climate change and environmental protection in the last two decades has raised the need for the development of new low-cost, chemical sensors suitable for use in online quality monitoring [1]–[5]. The scientific community has reacted dynamically to this challenge, as is evident from the increased number of publications and allocation of time in sensor conferences and chemical sensor research [6]–[9]. In particular, electrochemical, ion-selective electrodes (ISE) have received major interest featuring novel sensing structures for various chemical parameters, which have been developed using widely disparate technologies ranging from fibre optics to micromachining [10]–[12]. Mostly electrodes of the second kind are used as Reference Electrodes (REs). Ag/AgCl REs are widely used due to their environmental compatibility. The Mercury/Mercury Chloride (Hg/Hg_2Cl_2), calomel electrode, has advantages with regard to potential stability and light inertness, but has an upper temperature restriction of approx. 80 °C. Furthermore, mercury presents several environmental hazards and its use is generally restricted to laboratory based tests. The calomel electrode is still commercially available, in comparison to the Thallium(Mercury)/Thallium Chloride (Tl(Hg)/TlCl), the Thalamid™ electrode, which has been banned because of its toxicity [11]. An overview of the classical RE was given by Ives and Janz [13] while Kaden and Vonau [14] reported on electrochemical reference electrodes specifically for pH measurements and discussed advantages and drawbacks of single reference electrodes.

---

[*] Corresponding author. Tel.: +35799456318
 E-mail address: sophocleous.marios@ucy.ac.cy (Sophocleous M.)

The tendency to develop miniaturised electrochemical systems such as lab-on-chip and to make use of mass production, directs towards REs in a planar embodiment. Although a number of scientific approaches have been reported, with none of them proving successful for all the requirements, the traditional rod-shaped RE is still commercially dominant [11]. Several attempts have however been reported on the development of reference electrodes for ISFETs and silicon based substrates [15]–[20]. This paper provides a brief description of the construction and operation of the conventional Ag/AgCl RE and a comprehensive review on the advancements of screen-printed Ag/AgCl REs, not necessarily used for potentiometric sensors but that are suitable for implementation in potentiometric sensors. A combination of Thick-Film (TF) technology and electrochemical methods embraces the requirements of these devices by providing cost competitive solutions for the fabrication of compact, rugged and robust systems. TF technology offers several alternative solutions and allows flexible design with a wide range of materials, mass production and cost reduction through economies of scale [5]–[8], [21]–[26]. Other approaches such as ink-jet printing, thin-film technology, spraying, heat sealing, conducting polymers, semi-permeable membranes and microfabrication have been reported but have yet to achieve the same level of reliability as the conventional silver/silver chloride (Ag/AgCl) RE [27]–[34]. Several reviews have been published on general techniques with all-solid-state REs with satisfactory results but elevated cost [35], [36]. It is our belief that TF technology may be able to overcome some problems of the conventional REs. There are many standard types of REs which most commonly include some 'wet chemistry' in the form of an electrolyte solution that is required for their operation. Implementing such electrolyte regions within new sensor designs as an in-line manufacturing step has been proven to be a stumbling block for more than a decade [15], [37]–[41].

Generally, ISEs are used in potentiometric sensors which are made up of an ISE and a reference electrode (RE) pair. Usually, the potential difference between the two electrodes is proportional to the parameter to be measured [21], [42]–[44]. Publications are mostly focused on improving the performance of the ISE or inventing new and improved ISEs but it is recognised that the real challenge of a solid state potentiometric sensor is the RE [4]. This is the most essential element in any potentiometric measurement system since the response of any other type of ISE is meaningless without a reference to compare against [11], [45], [46]. From the point of electrochemistry, the thermodynamically defined, classical reference electrode is a special electrode (also called half-cell) featuring a reversible electrode reaction and a stable electrolytic contact to the analyte. That reversible reaction results in a distinct and stable electrode potential [47], [48], [49]. Although scientific interest is primarily dedicated to ISEs, improvements to the reference electrode have also been reported [11], [50]–[53].

2. Conventional Ag/AgCl reference electrode

2.1 Construction of the conventional Ag/AgCl reference electrode

The most common type of silver-silver halide electrode is the Ag/AgCl due to the availability of silver chloride and the use of potassium chloride as the electrolyte. The electrode is constructed using a silver wire, electroplated with silver chloride and then immersed into a 3.5 M or saturated potassium chloride (KCl) solution. The electrolyte is generally contained in a glass tube having a porous glass frit at the tip to allow ion exchange at the liquid-liquid junction. The conventional silver/silver chloride reference electrode has a relatively simple construction. A typical construction of such an electrode is shown in Figure 1.
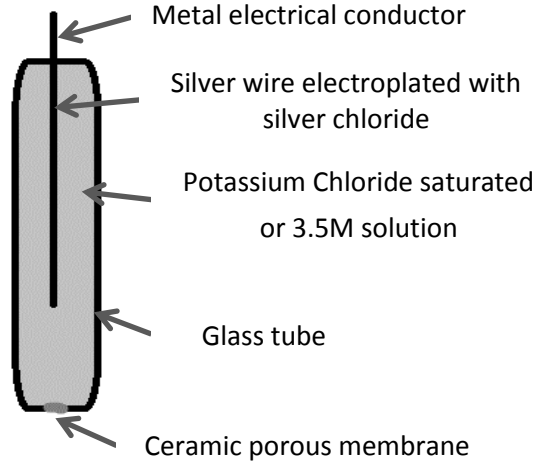
Figure 1: Typical construction of a silver-silver chloride reference electrode [1].

Potassium chloride is generally chosen as the electrolyte because both chloride and potassium ions have high ion mobilities of approximately equal value. This ensures a low-impedance path for ionic current between the internal and external test solution. The high ion mobilities improve the transient response characteristics of the whole reference electrode. The ratio between Ag and AgCl is an important parameter and according to [1] should ideally be approximately 4:1.

2.2 Operating principle of conventional Ag/AgCl reference electrode

The operating principle of the reference electrode is based on two simultaneous, reversible reactions on the surface of the electrode which is in contact with the solution [13]:

$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \tag{1}$$

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightleftharpoons AgCl_{(s)} \tag{2}$$

The electrode potential is defined by the Nernst equation, which is modified for this specific electrode for moderate chloride concentrations as [13]:

$$E = E^o - 2.303 \frac{RT}{nF} log([Cl^-]) \tag{3}$$

where E^0 is the electrode standard potential (a constant) (V), n is the number of electrons involved in the electrochemical reaction, R is the molar gas constant (J K^{-1} mol^{-1}), T is the absolute temperature (K), F is the Faraday constant (C mol^{-1}), [Cl$^-$] represents the concentration of free chloride ions (M). The electrode potential can be considered to be proportional to the chloride ion concentration at moderate concentrations. The term 2.303(RT/nF) is temperature dependent and thus the Ag/AgCl electrode in theory, exhibits a typical susceptibility of -59.16 mV/pCl at a temperature of 25°C. The surrounding electrolyte in the classic reference electrode design, serves to maintain a constant [Cl$^-$], usually by using a 3.5 M or saturated KCl solution.

Further details on the operating principle of the classical Ag/AgCl RE can be found elsewhere [13], [42], [43], [47], [48].

3. Screen-Printed Ag/AgCl reference electrodes

3.1 Description & requirements of a screen-printed Ag/AgCl reference electrode

Although the stability and performance of the classical construction is accurate to approximately a millivolt, it cannot be used in applications where robustness and ruggedness are required. In the case of soil sensors in a high-density sensor network, the use of a glass electrode is not preferred due to its glass-based construction and the porous frit and also because the electrodes are very expensive, typically more than a hundred euros each. That by itself defies the purpose of low-cost electrochemical sensors. A solid state, low cost, rugged, robust and accurate reference electrode is required and this is the gap that the screen-printed reference electrodes seeks to fill. A general imperfection of the conventional RE is tightly connected to the use of aqueous solutions and liquids more generally. The activity of potential-determining ions can fluctuate due to leakage of inner electrolyte via the interface of the RE and the solution it is immersed in. In order to avoid the contamination of the analyte by the reference electrolyte, a bridge electrolyte is sometimes used, usually called a double junction RE [11]. The reference electrolyte must necessarily not react with components in the solution to be analysed. Subsequently, the concentration and composition in the reference electrode itself and in its surrounding area may remain generally unchanged. A diaphragm, a porous frit, a ceramic fibre or a fine porous membrane controls the flow of electrolyte through the liquid–liquid junction. On the other hand, the outlet can be blocked by materials in real analytes such as in biological systems. REs have to meet several, rather demanding, requirements. They must be of low-cost, maintain a stable and reproducible potential even after a small electric current flow, their potentials must be unaffected by the composition of the analyte, meaning they are not influenced by pH value, concentration of redox species and dissolved oxygen, etc [16].

Honeychurch et al. in 2003 [54], published a review describing then current developments in the design and fabrication of disposable screen-printed sensors for the electrochemical determination of trace metals in biological, environmental and industrial samples. Although the paper focused on the specific fabrication methods and operational details of the ISEs and other types of working electrodes, in almost every one of the reported sensors a Ag/AgCl RE or QRE was used, further emphasising the importance of the RE. In that paper, Palchetti et al. described a printed pseudo-reference electrode on a polycarbonate strip but then concluded that the most important factor affecting the performance of the sensors was the stability of the reference electrode. The authors then performed their experiments in a KCl solution to stabilise the potential of the reference electrode, something that is essentially another way to move from a pseudo-reference electrode to a normal RE without removing the need for a liquid junction. These instances illustrate the differences in advancements between solid-state, screen-printed ISE and screen-printed RE. While the numbers of screen-printed ISE have grown exponentially, screen printed REs still have a long way to go to meet the technological demands of our times.

The term low-cost is very often used in literature but the truth is that what is high or low-cost depends greatly on the application. Of course, the return of installing these sensors should always be higher than the capital investment within a period of a couple of years. In centralised water quality monitoring systems for example, where a small number of sensors is required for very large amounts of water, the price of the sensor can be accepted to reach more than several hundreds of euros. In the case of environmental or agricultural sensors where a high-density sensor network is required, if the price of each sensor is several hundreds of euros, then the whole system will have a huge capital investment with the return rate to be more than seven or eight years, which is well beyond typical sensor lifetimes, making the system unsuitable for such applications. For this type of applications, the sensors cost should not exceed several tenths of euros in order to make their use feasible. The thick-film devices reported here are approximately an order of magnitude cheaper than their macroscale equivalents and are implemented on the same principle as the conventional electrolyte-filled Ag/AgCl reference electrode.

Generally screen-printed REs attempt to mimic the operation of the conventional RE through the immobilisation of salt reservoirs in the form of salt matrix layers fabricated as upper layers of a planar design

that are in contact with the analyte. Screen-printed REs consist of three functional layers, each one serving a different purpose. The first layer is the conductor layer, which is responsible for allowing electron transfer to close the electrical circuit. The second layer is the ion-to-electron layer, silver/silver chloride layer in this type of RE, that is responsible for interacting with ions and generating electron flow based on that interaction. This is the layer that is responsible for the potential of the electrode as explained by equations (1), (2), and (3) above. The last functional layer is the KCl layer that is responsible for controlling the chloride ion concentration around the electrode. These three layers are the same functional parts of the conventional liquid-filled RE. The main difference for the screen-printed RE is that those parts are in the form of layers with the functional materials incorporated in the printing inks used. Additional layers are required for the construction of the screen-printed RE in order to control the area of those functional layers exposed to the solutions and to protect the electrical connections.

The performance of a screen-printed reference electrode is generally described by its potential stability, lifetime, drift rate, hydration period, shelf-life and price. The potential stability of a screen-printed reference electrode is described by the number of ions or other substances influencing the operation of the electrode. In the case of the Ag/AgCl reference electrode, it is explained above that the potential of the electrode is directly affected by the $[Cl^-]$ and $[Ag^+]$. Although this type of reference electrode is widely considered to be very selective there are other ions such as $[F^-]$ that can interfere with its electro-potential. Therefore, characterisation on which substances affect the potential of the electrode is of primary importance. Furthermore, the degree of influence of each substance is a vital parameter in the characterisation of the potential stability. Reference electrodes might show higher susceptibilities to certain substances and lower to others. Knowledge of those susceptibility values are very important in order to identify which reference electrode is better to use for each application. The lifetime of a reference electrode is defined as the useful operating time of the electrode during which it maintains its described behaviour. Again, depending on the application the required lifetime of the electrode can typically range from a couple of minutes to a year. For example, in analytical chemistry if the electrode is disposable, its lifetime can be of several minutes but for environmental sensors, its lifetime should be a minimum of several months. Drift rate of the electrode is defined as the rate that its potential changes in constant conditions i.e. in the same solution. Ideally, drift rate should be as low as a few µV/day but once more this is application dependent. The hydration period for a screen-printed reference electrode is defined as the time required for the electrode to reach a stable potential when placed in a solution. Hydration period should be as short as possible and depending on the application can range from several seconds to several hours. Shelf-life of an electrode is defined as the maximum allowable time for an electrode to stay on the shelf after production and maintain its characteristics when placed in a solution. Screen-printed reference electrodes usually have more than a year of shelf-life while the liquid or gel-filled reference electrodes have less due to water evaporation [6]–[8], [25], [45].

A review concerning solid-state REs was published by Guth et al. in 2009 [11]. In their review, the authors included studies of planar, screen-printed QREs and REs. The authors described several issues with planar reference electrodes and presented some solutions to the problems either using Thick-Film or Thin-Film technologies. Most attempts presented here were focused on ways to maintain a stable chloride concentration on the reference electrode. It was illustrated that for a long lifetime, a large quantity of KCl solution has to be placed on the electrode in a very limited volume. Another important aspect illustrated here was that for a low electrode resistance there should be an appropriate exchange of charge carriers between the inner solution and the analyte. Furthermore, the reference electrode should be storable for a long time without aging and immediately ready for use. Different strategies have been pursued to overcome those challenges. Enhancing the lifetime of the electrodes means to control the diffusion of KCl from the electrode to the analyte. Several ways were used to overcome this issue by dissolving KCl in polymeric or glass based inks, by using hydrogels, or by printing several types of membranes on top of the KCl solution.

Reported membranes were based on PVC with ionic liquids, Nafion™, cellulose acetate, polyurethane, silicon rubber and water repellent layers. A disadvantage of present ionic liquid-based reference electrodes is their loss of ionic components in the sample solutions and the influence of hydrophobic and multivalent ions on their performance. Another approach was to minimise the contact area between the electrode and the analyte. This works well with the long term stability but it dramatically increases the hydration time of the electrode. Another strategy was to provide a much longer channel for the chloride ions to move when moving from the electrode into the analyte. Although this also works well with the long term stability, it greatly increases the impedance of the electrode. A further approach was reported that involved the deposition of the KCl reservoir on both sides of the AgCl layer allowing a larger amount of KCl to be printed on the electrode.

3.2 Quasi-reference electrodes

A pseudo-reference electrode is defined as "An electrode through which no appreciable current is allowed to flow and is used to observe or control the potential at a working electrode. A pseudo-reference electrode, such as a Ag wire, fulfils the role of a reference electrode but the electrochemical processes allowing it to do so are not well understood, in contrast to a true reference electrode" [55]. Essentially, any ISE can be used as a pseudo-reference electrode if it maintains a stable potential under specific conditions i.e. in a known medium.

In the case of Ag/AgCl QREs, the main difference between them and the normal Ag/AgCl reference electrodes is that the [Cl$^-$] is not maintained by a layer of constant [Cl$^-$] making the electrode susceptible to fluctuations of its electro-potential when the [Cl$^-$] varies. Looking at the general structure of a RE, a QRE consists of only 2 functional layers, the conductor and the ion-to-electron layer. The KCl layer (salt matrix, see Figure 2) used in the RE is not used at all in this type of electrode.
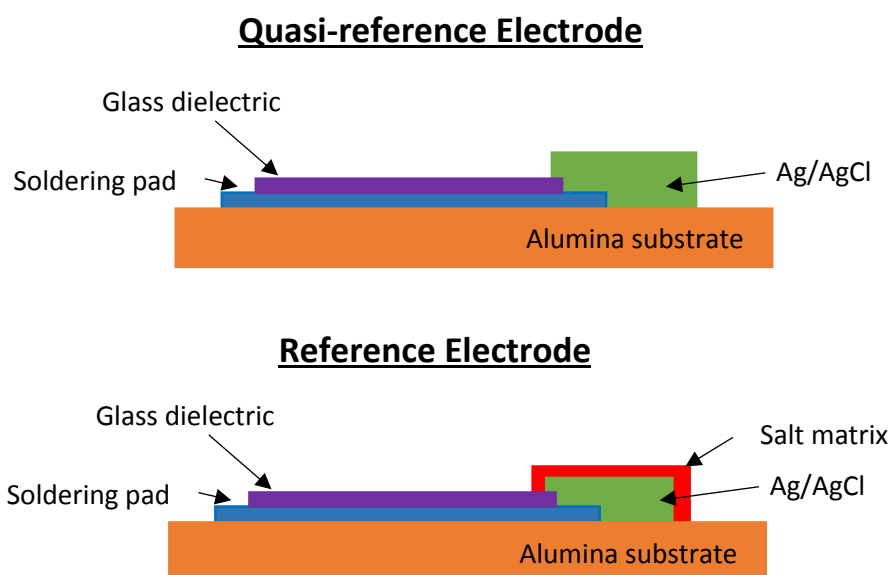

Figure 2: Difference between a QRE and a RE [10].

Usually, Ag/AgCl quasi- or pseudo-reference electrodes are limited to laboratory use due to their high susceptibility to [Cl$^-$] and [Ag$^+$] ions. In real-life examples such as environmental sensors, they are not used at all since proteins or other anions can greatly interfere with their electro-potential stability. Furthermore, QREs are more often used for voltammetry or amperometry since the medium is mostly known in those cases but in the area of sensors and analytical chemistry using potentiometry, the requirements for a reference electrode are much more demanding [56].

A wide variety of voltammetric, amperometric and potentiometric sensors have been reported that implement QREs while they have also been used in cyclic voltammetry. The construction and fabrication of Ag/AgCl QREs has been achieved by different approaches and on several different types of substrates, each one serving the specific application [49], [57]–[61]. Choi et al. in 2001 [62], developed a screen-printed disposable sensor for the anodic stripping voltammetric (ASV) analysis of heavy metals. The sensor comprised a mercuric oxide (HgO) working electrode, a Ag/AgCl QRE and a carbon counter electrode printed on a polycarbonate strip. The QRE was screen-printed using commercial silver ink, which was modified with fine AgCl powder. Andreescu et al. in 2002 [63], reported a screen-printed biosensor for the detection of pesticides in water miscible organic solvents. Although the major section of this work was focused on the development of the complete biosensor, a screen-printed Ag/AgCl RE was also employed. The fabrication technique was based on consecutive depositions of commercial Ag and AgCl inks printed on a plastic sheet. Glasspool et al. in 1998 [64], reported an amperometric dissolved oxygen sensor that implemented a screen-printed QRE printed using commercial inks on an alumina substrate. Guan et al. in 2005 [65], developed a disposable electrochemical biosensor for glucose monitoring. The QRE was printed on a PVC film again using commercial inks. In this case, the Ag/AgCl layer only covered the area of the electrode that would come in contact with the medium under investigation while the rest of the silver layer was used for soldering. Tangkuaram et al. in 2007 [66], again printed the QRE on PVC films with commercial inks for the development of disposable sensors using screen-printed carbon electrodes (SPCE). Carrara et al. in 2008 [67], demonstrated the development of a cholesterol biosensor, which incorporated a screen-printed Ag/AgCl but used cyclic voltammetry as the sensing method. Trivedi et al. in 2009 [68], developed a potentiometric urea sensitive biosensor, using a NH^{4+} ISE in double matrix membrane (DMM) technology as the transducer. In this study, another screen-printed Ag/AgCl QRE was developed. In this case, the Ag/AgCl paste was screen printed on a Melinex sheet of 150 μm thickness using a screen with a screen mesh size of 68 μm. Musa et al. in 2011 [23], described the development of a potentiometric, miniaturised, screen-printed pH sensor. The sensor comprised a screen-printed Ag/AgCl QRE that was coupled to a solid-state ISE. The work was mainly concerned with the optimisation of the materials and fabrication processes to make the sensor compliant with biomedical specifications. The authors achieved a sensor lifetime of more than 7 days by curing the Ag/AgCl pastes for 20 minutes at 120 ^{o}C after printing, which allowed the QREs to display excellent potential stability, as demonstrated by an open-circuit-potential standard deviation of ±1.2 mV over a period of 7 days (n=3 samples). The final device included both the QRE and the pH-electrode, and displayed an average pH sensitivity of -60.8 ±1.7 mV/pH, over a pH range of 7.00 to 7.63. Although these results are quite promising, the pH range of 7 to 7.63 is relatively narrow for environmental applications and even for analytical purposes. The fact that the sensor is using a QRE is not ideal for application in media with wide variations. This illustrates further the important of a reliable reference electrode since the major performance issues with this pH sensor were due to the reference electrode and not the ISE.

All of these approaches that used QREs could have been more successful and the sensors described used in a wider range of mediums if a true RE existed that had a satisfactory performance. This further highlights the importance of a miniaturised and reliable RE because of the wider range of applications that it can have.

3.3 Reference electrodes

3.3.1 Understanding the factors affecting the performance of REs

Atkinson et al in 2011 [46], demonstrated the importance of fabrication parameters on the performance of screen-printed REs. Several types of REs were investigated with the main area of focus being the KCl weight ratio in the top KCl matrix. In this study, two types of pastes were used. One of them was a commercial, polymer-based ink and the other on was an in-house gel. The construction of the electrode was similar to the one previously reported by Cranny and Atkinson [45] with the main difference being the KCl concentration in the salt matrix layer. The authors concluded that although a trade-off exists between

hydration times and drift rate, which is dependent on device thickness, the initial salt concentration levels and binder type also have a significant effect on the RE's lifetime. As the thickness of the KCl matrix increases, the REs take longer to hydrate but exhibit longer lifetimes in a given range of chloride solutions. Furthermore, the RE's stability and response time is also influenced by the binder type used in the final salt reservoir layer.

Prasek et al. in 2008 [69], presented a very interesting paper at the 31st International Spring Seminar on Electronics Technology: Reliability and Life-time Prediction. Their paper presented the performance variations due to different Ag/AgCl pastes used on the REs. Although in this paper, the experiments were not performed in a [Cl⁻] controlled environment, the results of this paper are vital to understand the effect of fabrication differences of the Ag/AgCl layer. They used various commercial Ag/AgCl pastes with different Ag:AgCl ratios and they also investigated the performance of an electroplated Ag electrode using a KCl solution of pH 2 hydrochloric acid. The QREs were tested using cyclic voltammetry and it was found that both commercial (DuPont) pastes had similar current response although the Ag:AgCl ratio was different. Comparing the QREs with the conventional Ag/AgCl RE, the current response was found to be comparable but with a shift of half-wave potential in the range of approximately 100 mV. The electrochemically fabricated QRE has similar half-wave potentials to the DuPont paste ones, but the peak current during the reduction process was higher. Finally, they suggested that for planar electrodes, the commercial DuPont pastes were better due to their high reproducibility. Additionally, it was shown that the Ag:AgCl ratio did not affect their performance with respect to the cyclic voltammetry experiments but none of the rest of the parameters such as chloride susceptibility, hydration time or lifetime were investigated.

Atkinson et al. published a paper in 2013 [12] reporting thick film environmental and chemical sensor arrays designed for deployment in both subterranean and submerged aqueous applications. Various choices of materials for reference electrodes employed in these different applications were evaluated and the responses of the different sensor types were compared and discussed. Interestingly enough, after a simple fabrication mistake, it was realised that REs without the Ag/AgCl layer had a much lower susceptibility to Cl⁻ concentration for a certain period of time. After that, they tended to behave very similarly to the rest of the Ag/AgCl REs. Also, different types of binder (glass and polymer) were tested for the Ag/AgCl layers. The addition of another layer on top of the KCl containing salt matrix layer was found to provide a better stability in varying concentrations of KCl test solutions. The authors concluded that through the careful choice of materials, it is possible to fabricate thick-film electrochemical sensors that are suitable for a variety of different application areas. For short-term deployments in water where chloride ion concentrations are liable to wide variation, it may be preferable to employ a reference electrode without the Ag/AgCl layer and trade off a higher rate of drift for immunity to chloride ion concentration variation. In these short term deployments a single point calibration can more easily be employed to compensate for the electrode drift. On the other hand, for longer term deployment it would appear preferable to employ a device with a thicker silver/silver chloride layer, resulting in an increased sensitivity to chloride ion concentration variation but a lower long term potential drift. Experimental results indicated that the choice of binder materials is critical to the production of sensors capable of medium term deployment (e.g. several days) as the binder composition not only affects the trade-off between hydration time and drift but also has a significant bearing on device sensitivity and stability. Sensor calibration was shown to remain an issue for long-term deployments (e.g. several weeks) but this could be ameliorated in the medium term with the use of novel device fabrication and packaging techniques. The reported results indicate that is possible through careful choice of materials and fabrication methods to achieve near stable thick film reference electrodes that are suitable for use in solid state chemical sensors in a variety of different application areas.

That same year, this group published another paper [10] on screen-printed Ag/AgCl REs reporting much more comprehensive experimental work. The group experimented with multiple commercial and in-house

Ag/AgCl pastes and with REs not having a Ag/AgCl layer. From previous work, it was found that REs without the Ag/AgCl layer could be made less susceptible to Cl⁻ concentration and a set of experiments was designed to understand the reasons behind it. Scanning electron microscopy (SEM) studies were performed on the electrode's cross section and it was found that when the top KCl matrix was printed, even before immersing the REs in solutions, the bottom silver layer formed a very thin AgCl layer. Furthermore, different binders were used to formulate the Ag/AgCl pastes, something that was shown to affect the behaviour of the REs. The authors further experimented with several different KCl to binder weight ratios in the KCl matrix layer. They further printed an extra KCl matrix on top of the first one with varying KCl weight ratios in an attempt to find a way to hold the KCl on the electrode for longer time. The best performances in terms of chloride susceptibility were obtained by REs without the Ag/AgCl layer and with two KCl matrices of approximately 50 wt% and 0 wt%, respectively. The reported chloride susceptibility was less than ±2 mV/decade of Cl-, which compared to the typical sensitivity of a pH ISE of approximately 59 mV/pH, translated to a reading error of less than ±0.1 pH. These REs were further tested in pH buffers of 3, 7 & 10 and showed a susceptibility of less than ±5 mV in this range.

In 2012, Sophocleous et al. [70] presented a paper at the IEEE Sensors conference, showing the fabrication parameters' effect on the REs performance in terms of lifetime and Cl⁻ susceptibility. These REs were screen-printed using commercial inks with the top layer being a KCl bound matrix. Different variations of KCl to binder weight ratios (20%, 50% and 66% ratio by weight) were investigated with an additional layer of a commercial polymer-based paste deposited on top of the KCl matrix (figure 3).
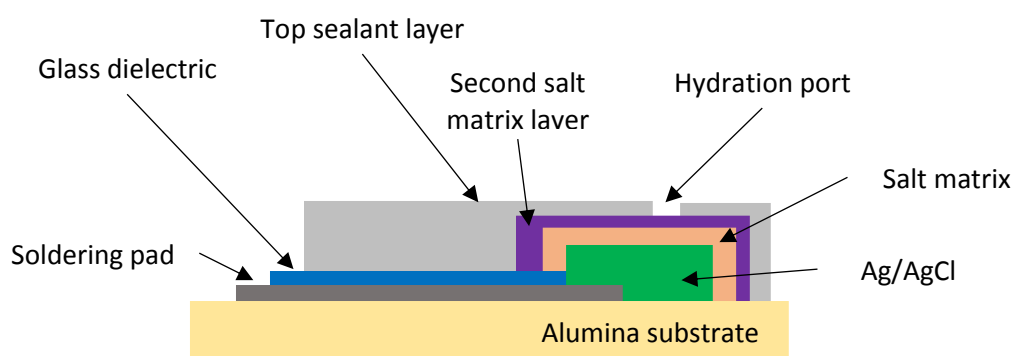

Figure 3:   Cross section of the reference electrode with an additional salt matrix layer [70].

These electrodes provided significant stability in terms of Cl⁻ susceptibility of less than ±2 mV/decade of [Cl⁻]. It was further suggested that these Thick-Film REs can be suitable for use in underground soil measurements.

From the pre-mentioned papers, it is now understood that although a trade-off exists between hydration times and drift rate, which is dependent on device thickness, the initial salt concentration levels in the top salt matrix/electrolyte layer and binder type also have a significant effect on the RE's lifetime. As the thickness of that layer increases, the REs takes longer to hydrate but features longer lifetimes in a given range of chloride solutions. The stability and response time of the REs is also influenced by the binder type (ink) used in the final salt reservoir layer. In addition, for planar electrodes, the commercial pastes silver/silver chloride pastes are better due to their high reproducibility. Additionally, the Ag:AgCl ratio does not affect the RE's performance with respect to cyclic voltammetry experiments. From the work of Glanc-Gostkiewicz et al. in 2013 [16], it was found that an extra layer of polymer based ink (ESL 242SB) on top of the electrolyte layer has a significant effect on the lifetime of the electrodes since it can greatly affect the diffusion rate of the electrolyte from the electrode to the solution. Furthermore, through the careful choice of materials, it was found that it is possible to fabricate thick-film electrochemical sensors that are suitable

for a variety of different application areas. For short-term deployments in water where chloride ion concentrations are liable to wide variation, it may be preferable to employ a reference electrode without the Ag/AgCl layer and trade off a higher rate of drift for immunity to chloride ion concentration variation. In these short term deployments a single point calibration can more easily be employed to compensate for the electrode drift. On the other hand, for longer term deployment it would appear preferable to employ a device with a thicker silver/silver chloride layer, resulting in an increased sensitivity to chloride ion concentration variation but a lower longer term potential drift. For example, this would be applicable for subterranean soil deployment where KCl levels were not expected to vary widely. The results indicated that the choice of binder materials is critical to the production of sensors capable of medium term deployment (e.g. several days) as the binder composition not only affects the trade-off between hydration time and drift but also has a significant bearing on device sensitivity and stability.

3.3.2 Disposable electrodes

Mroz et al. in 1998 [71], reported a disposable reference electrode that was developed for use in environmental and medical analysis. The electrode's structure differed from the previous ones as this electrode did not contain an Ag layer and the connection to the potentiometer was made directly from the Ag/AgCl pad. The Ag/AgCl layer was printed onto the sealing film, which was the lamination material. On top of the Ag/AgCl layer and until the end of the sealing film, a glass-fibre medium was printed and sealed with another laminating layer on top (figure 4). The ion exchange between the Ag/AgCl and the testing solution was therefore achieved only through the glass-fibre medium that was filled with KCl electrolyte.
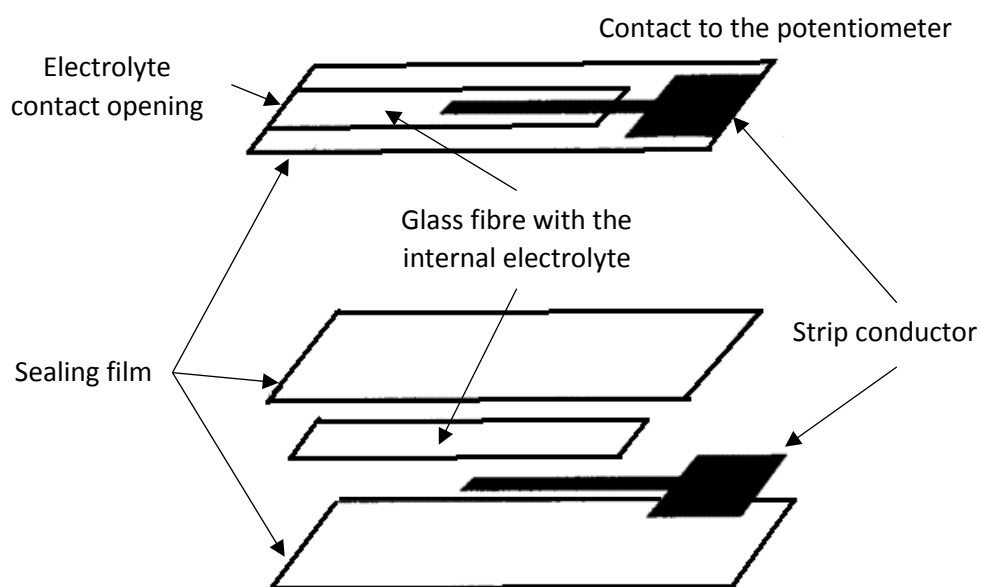

Figure 4: Schematic view of the disposable reference electrode [71].

It was found that the potential difference between this electrode and a commercial electrode was hardly influenced by chloride concentration changes over the range pH (3–11) of the analyte solution. This electrode featured a shelf life of more than 10 weeks while the operational lifetime of the electrode was more than several hours.

Jeonghan Ha et al. in 2005 [72], presented a paper concerning screen-printed REs (figure 5) that were fabricated with two types of polymeric membranes composed of 30 wt.% cellulose acetate (CA) and polyurethane (PU). The REs were developed for the fabrication of mass producible solid-state reference electrodes. The choice of CA/PU membranes was made due to the properties of the materials to properly adhere on common substrates (e.g., ceramic and silicon chips) of miniaturized electrochemical sensors and

further allow for rapid hydration of the internal hydrogel layer (3M KCl with a 6 wt.% water soluble polymer). The internal hydrogel layer was deposited on the micro-patterned electrodes.
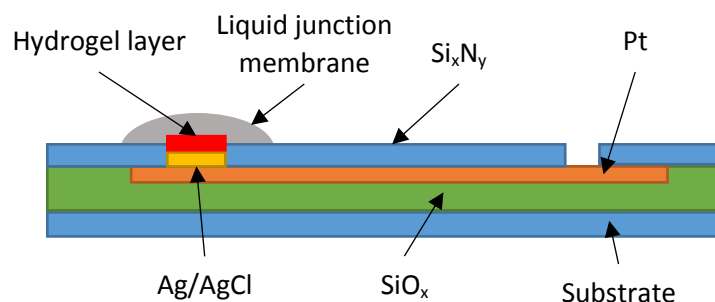

Figure 5: Polymer membrane-based reference electrodes on silicon substrate [72].

This structure featured a fast preconditioning time of approximately 100 seconds and a stable potential for an extended lifetime of approximately 25–90 minutes. That was achieved by limiting the diffusion of internal electrolytes. The potentiometric responses of the CA/PU membrane-based solid-state REs drifted rapidly by 40–90 mV/h after their end of lifetime, which suggests that the internal electrolyte slowly flows through the micro-channels of the outer membrane during the lifetime of the electrode and then diffuses away in the solution at an increased rate. The REs were tested against other membrane-based ISEs and their performances closely matched that of sensors whose potentials were measured versus the conventional RE. Although the REs' performances were satisfactory in this study, the lifetime of the electrodes at approximately 25-90 minutes is poor compared to the typical lifetime of the conventional RE of more than a year.

Idegami et al. in 2010 [73], developed a low-cost, Ag/AgCl RE using screen-printing technology and investigated its performance against the conventional Ag/AgCl RE. The electrode's structure consisted of a layer of glass-epoxy substrate, a layer of conductive track, a layer of Ag/AgCl, a layer with an internal electrolyte, an insulating layer with two slits and a hydrophilic polymer-coated polyester film (figure 6). The internal electrolyte was prepared as saturated KCl in 2% sodium alginate. The surface of the alginate layer was gelated by applying 3 wt% $CaCl_2$ solution. Two slits were made in the insulating layer; one slit was made to allow the test solution to come into contact with the inner component of the RE and the other was made to allow air to escape. Finally, the RE was uniformly covered with a hydrophilic polymer-coated polyester film.
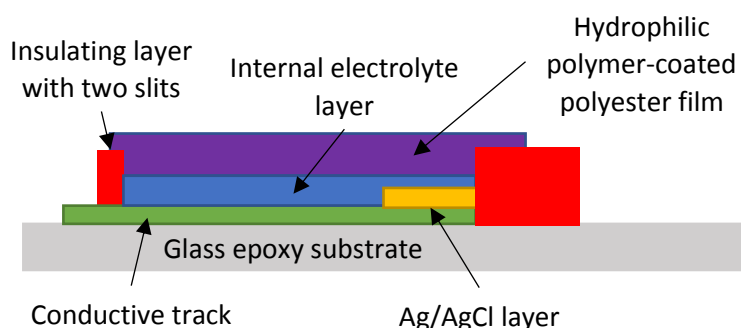

Figure 6: Cross section of the screen-printed reference electrode [73].

The RE had a long-term potential stability of approximately 60 min and its performance did not widely depend on Cl⁻ concentration.

Shitanda et al. in 2015 [74], reported a paper-based, screen-printed Ag/AgCl RE that featured a hydration time of less than a minute and a lifetime of up 75 hours. The RE was fabricated using a Ag/AgCl ink that was printed on one side of a water-repellent-treated paper substrate (figure 7). The thickness of the paper substrate was 800 µm. Then, the conducting layer of Ag was formed using a commercial Ag ink. The Ag and Ag/AgCl inks were cured at 120 °C for 20 min. Then, a resist ink was printed on top of the Ag layer to prevent the inner electrolyte (KCl) from releasing to the test solution, which was cured at 100 °C for 20 min. Next, 0.5 mL of a saturated KCl solution, solution, which was produced by dissolving 246 mg of KCl in 1 mL of ultrapure water, was dropped on the opposite side of the water-repellent-treated paper substrate three times. Then, a pattern was printed using a resist ink and dried at 120 °C for 20 min. Finally, the entire reference electrode (without the liquid junction and the Ag lead) was coated again with a water-repellent ink.
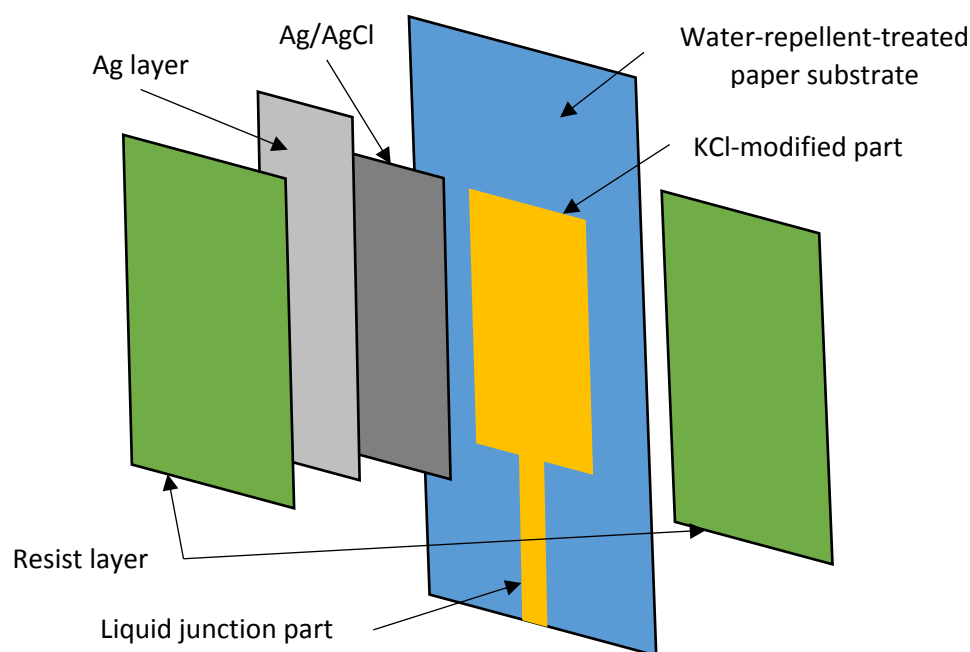

Figure 7: Schematic diagram showing the structure of the synthesized Ag/AgCl reference electrode [74].

The open-circuit potential of the reference electrode in a 0.1 M Na_2SO_4 solution was measured against a commercial saturated KCl/Ag/AgCl reference electrode. The initial potential of the reference electrode after immersion in the solution was approximately −4 mV. The open-circuit potential eventually became stable within 1 min. This result means that the paper liquid junction supplied enough volume of the test solution into the electrolyte layer within 1 min. The reference electrode was stable for approximately 75 h. After 75 hours, a potential drift to the positive side was observed. The rate of Cl⁻ ions effluxing from the RE was compared with the rate of Cl⁻ ions effluxing from a commercial Ag/AgCl. The synthesized electrode and the commercial reference electrode were kept immersed in ultrapure water, and the total number of effluxing Cl⁻ ions was determined through potentiometric measurements performed using a two-electrode system. A bare screen-printed Ag/AgCl electrode was used as the Cl⁻ ion sensor (i.e., the working electrode), while a commercial saturated KCl/Ag/AgCl electrode was used as the reference electrode. The average change in the number of Cl⁻ ions effluxing from the RE was 5.75×10^{-5} mol h⁻¹, which was slightly higher than the change in the number of ions effluxing from the commercial reference electrode (4.80×10^{-6} mol h⁻¹). This RE featured

very low hydration times and a reasonable lifetime for applications such as disposable sample analysis tools but has a long way to go for applications such as environmental monitoring.

In general, disposable electrodes require very fast hydration time for instant use, high potential stability in a wide range of Cl⁻ concentrations, the least possible interference from other ions, relatively low cost and the lifetime of the electrode can be as short as several hours. Several attempts have been described in this section with substrates ranging from paper-based to glass epoxy to silicon and heat-sealing films. These electrodes featured hydration times of several minutes with very low interference from any ions and lifetimes of more than a couple of days. Due to the fact that a perfect RE is not feasible currently, researchers try to implement different fabrication strategies with different materials to fulfil the requirements of their specific application instead of universally solving the RE issues.

3.3.3 Reusable electrodes

One of the first reported studies on screen-printed REs was conducted by Desmond et al. in 1997 [75]. The study involved two different types of micro reference electrode and their preparation method and performance was investigated. The first type of the RE was constructed by printing a Ag/AgCl ink on platinum that was already printed on silicon. The second RE type was identical to the first type but had an extra layer of a chloride doped vinyl ester resin (figure 8).
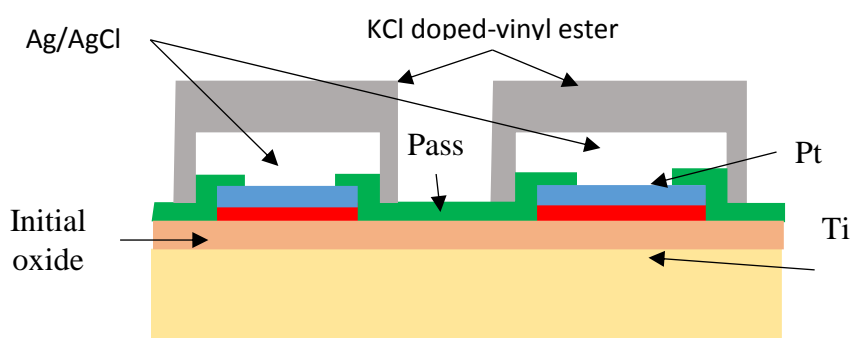

Figure 8:   Layout of the RE with the KCl doped-vinyl ester layer [75].

The second RE type was designed to eliminate the effect on electrode performance from chloride concentration variations. In this study, it was realised that the first RE type was acting as a chloride ISE with a sensitivity of -55.83 mV per decade of chloride activity. On the other hand, the second RE type showed a potential of -40.1 to -20.3 mV when measured against a standard calomel electrode (SCE) for KCl concentration range of 10^{-7} to 1 M, respectively. A commercially available macro-scale, solid-state RE that was fabricated from the same materials as this type of RE was also investigated. While type 2 RE showed a mean potential of -15.4 mV with standard deviation of 10.9 mV, the commercial macro-scale RE had a much more stable potential of -31.9 mV with standard deviation of 2.7 mV. Although the materials used for the development of both the macro-scale and the screen-printed RE were the same, their performances were very different. The screen-printed RE had almost five times higher standard deviation than the macro-scale equivalent. These results highlighted the presence of further challenges in the process to develop a screen-printed RE with similar performance as its macro-scale equivalent.

Cranny and Atkinson in 1998 [45], adopted a similar approach but instead of using a chloride doped vinyl ester resin, they attempted to KCl dope a commercially available screen-printing ink and to form a KCl salt matrix on top of the Ag/AgCl layer (figure 9). They further attempted to develop their own in-house inks and dope them with KCl to form the same KCl salt matrix. In addition, they tried to form their own in-house

Ag/AgCl inks with different binders, glass or polymer, to investigate the effect of those binders on the electrode's performance.
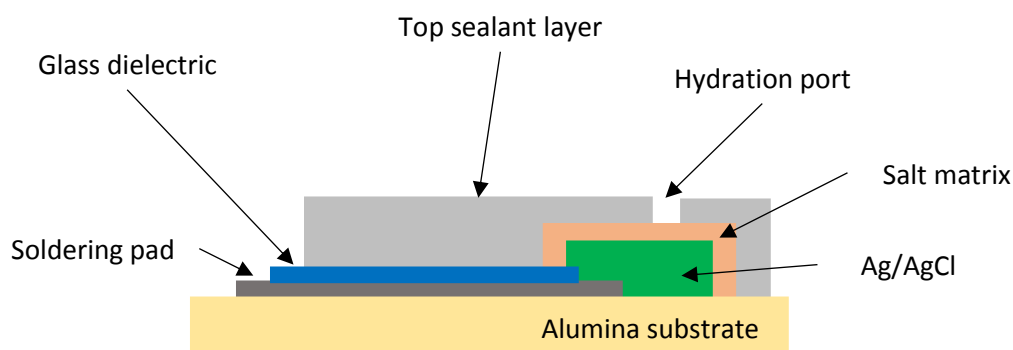

Figure 9:   Cross sectional view through a thick-film Ag/AgCl reference electrode [45].

The REs were tested for hydration time, chloride concentration susceptibility, lifetime, potential drift and shelf life. The results are presented in Table 1 below. The chloride concentration susceptibility was investigated before the deposition of the KCl salt matrix to ensure that the electrodes obeyed the Nernst equation. Differences between polymer Ag/AgCl and glass based AgCl pastes have a direct effect on the hydration time, potential drift, lifetime and shelf-life of the electrodes. Glass based AgCl layer with the polymer KCl salt matrix tend to have the longest lifetime with relatively low drift but they also have the longest hydration times. This suggests a trade-off between the hydration time and drift rate/lifetime of such an electrode.

Table 1: Performances of various REs with several construction variations. [45]

Ag/AgCl Paste	Cl ion susceptibility mV/log[Cl⁻]	Standard potential (mV)	KCl salt matrix	Hydration time (h)	Potential drift (mV day⁻¹)	Lifetime (days)	Shelf life (months)
Polymer Ag/AgCl	-61.24	-9.94	Polymer	6	6.8	25	>6
Glassy AgCl	-60.74	-9.99	Polymer	10	4.4	40	>12
			Glassy	5	6.0	14	>12
Glassy AgCl	-59.99	-5.88	Polymer	4	-	-	>12
			Glassy	1	4.2	20	>12

It is noteworthy to mention that the potential drift was measured over the lifetime phase when the salt loss is constant, the lifetime was calculated during the constant drift phase and the shelf life was calculated with the assumption that the REs were stored in a dry area.

Simonis et al. in 2003 [20], reported the development of an on-chip pH sensor comprising of a thin-film pH ISE and a thick-film Ag/AgCl RE (figure 10).
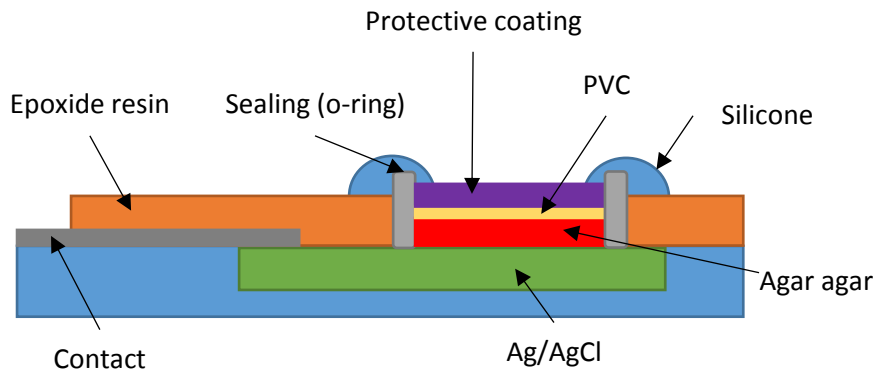
Figure 10: Cross section of the miniaturized reference electrode with KCL containing membrane and protective coating [20].

The thick-film reference electrode was integrated with a thin-film pH sensor onto one chip and the system (pH electrode/RE) was investigated by means of capacitance/voltage (C/V) and constant capacitance (ConCap) mode. The study further investigated the performance of different types of Ag/AgCl REs that have been fabricated by either thin- or thick-film technologies. In this study, KCl-containing membranes of various types were printed for inner electrolyte and different coatings were used to protect the RE from a fast leaching out of the KCl. It was found that the potential stability of the REs without KCl-containing membranes in KCl solutions of 3M was about 7 hours for thin-film electrodes and up to 90 hours for thick-film electrodes. In the case of the REs with the membrane, it was found that they exhibited a very stable potential for more than two months. About a year later, the same group (Simonis et al.) [76], published another paper showing their work on different types of reference electrodes that have been fabricated by thin-film (electron-beam evaporation/pulsed laser deposition (PLD) or electron-beam evaporation/chlorination) and thick-film techniques. In this further work, they showed how different coatings above the KCl-containing membranes can affect the KCl leaching rate. The average drift during a typical measurement time of 10 h was found to be less than 0.1 mV/h for the thick-film reference electrodes with cellulose nitrate employed as a protective coating, while the average drift rate of the thin-film reference electrodes was about 0.4 mV/h. These results provided significant advancement in terms of understanding the important factors affecting the performance of Ag/AgCl REs.

In 2004 Tymecki et al. [22], reported a convenient and reliable method for large-scale production of miniaturized, planar, all-solid-state REs. The REs were entirely fabricated with Thick-Film technology that allows a direct transfer to mass production with low cost. The pastes used were cured at low temperature to ensure low-cost and simultaneously allow the possibility for printing on plastic and flexible foils. The structure of the RE was very simple and consisted of a commercial polymer based Ag/AgCl paste with 3:2 ratio of Ag:AgCl, a KCl doped electrolyte paste and a commercial UV cured protective paste. The electrolyte paste was prepared by grinding the protective paste with finely powdered KCl with a weight ratio of about 30%. Then, the electrodes were screen-printed onto a flexible polyester foil 125 μm thick (figure 11).
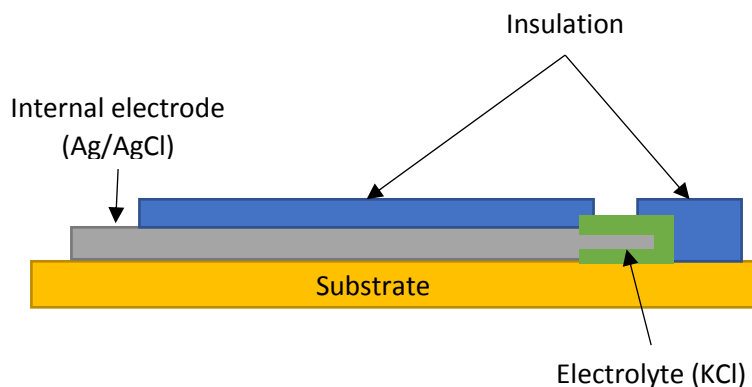
Figure 11:   Schematic of the investigated reference electrodes [22].

The developed REs exhibited an improved long-term stability with continuous operational life-time in excess of one week. Shelf life was longer than 9 months and several important test solutions (pH, chlorides as well as other halide anions, typical buffer components, alkaline and heavy metal cations, complexing ligands and redox agents) did not significantly influence the potential of the REs.

Martínez-Máñez et al. in 2005 [5], published a paper regarding the use of a sensor array for water quality monitoring. That sensor array consisted of several sensors to measure pH, temperature, dissolved oxygen, conductivity, redox potential and turbidity. The sensor array was fabricated using thick-film technology, using mostly commercially available serigraphic pastes. The sensor array has the ability to be implemented with in-situ portable or stationary instrumentation for water quality monitoring. The RE used on this sensor array was based on the classical structure of Ag and Ag/AgCl layer. These REs further implemented a membrane based layer that was doped with KCl at various weight percentages. The membrane layer contained finely divided crystalline KCl concentrations of more than 15%. The best performances were achieved by the REs incorporating the dielectric paste D2020529D1 from GEM Limited, the encapsulating resin EPOTEK H77 and a simple membrane made with polyisophthalamide diphenylsulfone (PIDS). These electrodes featured a stable potential without drifting for more than a month.

Liao and Chou in 2006 [77], presented a planar, solid electrolyte modified, (PSEM) Ag/AgCl RE that was fabricated using Thick-Film technology. The authors used agar gel as the inner electrolyte and chloroprene rubber for the liquid junction and insulator (figure 12). These materials were chosen based on their low cost and simple fabrication using the technique of screen-printing. It was suggested that these REs were ideal candidates for cost-efficient mass production.

Figure 12:   Schematic illustration of the PSEM Ag/AgCl reference electrode [77].

The paper showed that the developed RE was insensitive to most of the physiologically important ionic species, including Na^+, K^+, Li^+, Ca^{2+}, $NH4^+$, and Cl^-, under continuous measurement conditions. These electrodes have the same behaviour as the rest of the screen-printed electrodes, meaning that they maintain a stable potential for as long as the electrolyte is held below the membrane and the gel is hydrated.

The PSEM Ag/AgCl RE was further integrated with an iridium oxide modified Pt-based pH ISE as a complete on-chip pH sensor. The performance of the complete sensor was very much comparable with that of the sensor with a conventional RE.

Mamińska et al. in 2006 [78], published their work that included the development of an all-solid-state, miniaturised RE suitable for flow-through analysis (figure 13). The RE was based on Ag/AgCl planar microelectrodes covered with PVC membranes containing an ionic liquid (IL, 1-dodecyl-3-methylimidazolium chloride). This work is another example of the many attempts to hold the Cl$^-$ concentration around the Ag/AgCl layer constant. Several variations of different ionic liquid content in the membrane were investigated.

PVC membrane
Cu/Ag/AgCl layer
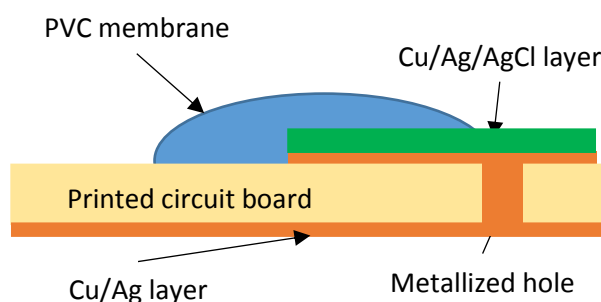Printed circuit board
Cu/Ag layer
Metallized hole

Figure 13:   Cross section of the reference microelectrode based on PVC membrane coating [78].

The REs exhibited a very promising performance in terms of potential stability of better than ±5 mV, reproducibility and long-term stability of more than 2 months. These electrodes were further utilised as REs in flow-cell measurements with potassium-selective planar microelectrodes. A comparison between the newly developed planar REs and a commercial Ag/AgCl RE was presented. The developed REs featured a very similar performance to that of the commercial RE with the main difference being their lifetime. These REs have been shown to have a lifetime of more than 2 months while a commercial RE has a lifetime of more than a year.

Shitanda et al. in 2011 [40], developed a screen-printed, planar, solid-state Ag/AgCl RE in which a poly(dimethylsiloxane) (PDMS) emulsion was utilised as the material to form the inner electrolyte layer and the liquid junction. The RE was fabricated as an attempt to further improve its potential stability. This technique provided some promising results with a lifetime of more than 2 months. Furthermore, the REs were tested for susceptibility to other important ionic species such as Na$^+$, K$^+$, Cl$^-$ and PO$_4^{2-}$, under continuous measurements and the results suggested that the potential of the electrode was almost unaffected by them. In addition, no significant difference in cyclic voltammograms was observed in 10 mM Na$_2$SO$_4$ solution containing 5 mM K$_3$[Fe(CN)$_6$] and K$_4$[Fe(CN)$_6$] with the present or a commercial Ag/AgCl RE.

A screen-printed, potentiometric sensor was reported by Glanc-Gostkiewicz et al. in 2013 [16] that utilised similar RE structures as the ones explained by Atkinson et al in 2013 [12]. This sensor was designed for deployment in remote catchment areas. 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. In this work, the group implemented a ruthenium oxide (RuO$_2$) ISE and a Ag/AgCl RE. Various choices of materials were evaluated for the fabrication of the thick-film pH sensors resulting in a device with a sensitivity of approximately 30 mV/pH at ambient temperature. The various REs employed here included the electroplating of a Ag layer in KCl solutions for different durations in order to vary the AgCl layer thickness. However, results suggested that the screen-printed Ag/AgCl layer was much more reliable in terms of reproducibility.

Alva et al. in 2016 [79], published a paper on the optimisation of SPREs based on charge balance and a poly(butyl acrylate) photo-curable membrane. In this more recent study, the authors attempted to replace the classical liquid junction solution with an ion-permeable-membrane as a means to create an all-solid-state electrode. The membrane was made up of a photo-curable acrylic ink that contained immobilised sodium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB) and trimethylocthylammonium chloride (TOMA-Cl). The optimum ratio between the two substances was found to be 1:1. The electrodes were tested for long-term stability in various concentrations of KCl solutions, for the effect of other anions in the solutions and then compared their performance with that of the classical gel-filled type. The stability of the reference electrode was determined by measuring its potential value in four different KCl concentrations (1 M, 0.1 M, 10^{-3} M and 10^{-6} M) at every hour for seven hours. For the initial five hours, the potential changes by 0.97 ± 0.04 mV/dec with a RSD of 3.95% while for the last 2 hours, the potential increased by more than 10 mV. It was suggested that this was probably caused by problems with a lipophilic salt component in the membrane, causing the charge in the membrane to become unbalanced. In this study, TOMA-Cl is used to increase the conductivity in the membrane layer. TOMA-Cl is an organic cation having a high lipophilicity. TOMA-Cl presence will cause the membrane to have a positive charge and this will subsequently force the anions to interact with it in the ion exchange process. The electrodes were tested for interference for Cl^-, NO_3^-, Br^-, SO_4^{2-}, and ClO_4^- with a concentration of 0.1 M to 10^{-8} M. The results are shown in Table 2.

Table 2: Influence of anion concentration on the electrode's potential.

Anion	ΔmV	R.S.D (%), n=3
Cl^-	5.40 ± 0.31	5.62
NO_3^-	8.40 ± 0.21	2.49
Br^-	8.00 ± 0.51	6.39
SO_4^{2-}	9.00 ± 0.40	4.47
ClO_4^-	173.20 ± 9.08	5.24

The only anion that significantly affects the potential of the electrodes is the perchlorate anion. It is believed that the interference is caused by the constant perchlorate increase in the dielectric membrane containing the ionic lipophile. Table 3 shows a comparison between the performance of the developed REs and the conventional Gel-filled used for a potassium and ammonium sensor.

Table 3: Comparison of the SP with the conventional Gel-filled reference electrode.

Sensor	RE	Linear Range (M)	Slope (mV/dec)	LOD (M)
K^+	SP RE	0.1-10-5	54.10 ± 0.60	(3.35 ± 0.64) x10-6
	Gel RE	0.1-10-5	56.10 ± 0.17	(2.70 ± 0.29) x10-6
NH_4^+	SP RE	0.1-10-6	52.10 ± 1.35	(4.92 ± 0.92) x10-7
	Gel RE	0.1-10-6	55.40 ± 1.04	(6.73 ± 1.54) x10-7

Although, overall slopes are close to the Nernstian response, the slopes of the sensors using SPRE were lower compared with the measurement standard reference electrode gel. This is likely made by the absence of an inner layer from SPRE which may stabilize overloading as found in the double junction RE.

A summary of the screen-printed reference electrodes discussed is provided in Table 4 for a better comparison between them. The table includes performance and fabrication differences highlighted with advantages and disadvantages and their suitability for certain applications.

Table 4: Performance comparison of reported screen-printed, Ag/AgCl reference electrodes (not QREs).

Construction	Experimental results	Pros	Cons	Ref.
Silicon substrate-Layer 1 Initial Oxide-Layer 2 Titanium-Layer 3 Platinum-Layer 4 Silver/silver chloride-Layer 5 KCl doped vinyl ester membrane-Layer 6	Mean potential of -15.4 mV with standard deviation of 10.9 mV for KCl concentration range of 10^{-7} to 1 M. In 10^{-5} M KCl, the electrodes showed a mean potential and standard deviation of −11.7 and 0.7 mV, respectively. The 10^{-7} and 10^{-1} M KCl solutions showed by far the greatest variation, with the latter being −38.5 mV after 1 minute and −8.5 mV after 15 min. The standard deviation associated with 10^{-7} M KCl was 11.5 mV.	Relatively low susceptibility to chloride (-15.4 mV/log[Cl⁻]) in a very wide range of concentrations (10^{-7} to 1 M)	Very unstable potential (up to -38.5 mV fluctuations after 1 minute in 10^{-1} M)	[75]
Alumina substrate-Layer 1 Silver-Layer 2 Silver/Silver Chloride-Layer 3 KCl mixed in polymer paste (Heraeus, IP027) at 50% ratio by weight-Layer 4	Obey Nernst equation with respect to chloride concentrations without layer 4 (59.99 to 61.24 mV/log[Cl⁻]), short hydration times (1 to 10 hours), drift rates of several mV (4.2 to 6.8 mV day⁻¹) with lifetimes of more than a month (14 to 40 days) and shelf life of almost a year (6 to 12 months).	Long shelf life of more than a year, long lifetime (14 to 40 days) for laboratory applications and hydration times down to a couple of hours (1 to 10 hours)	High drift rate (4.2 to 6.8 mV/day) and short lifetime for environmental applications (14 to 40 hours)	[45]
Sheet of heat-sealing film-Layer 1 Ag/AgCl with Ag:AgCl ratio of 3:2-Layer 2 Glass fibre with internal electrolyte-Layer 3 Sheet of heat-sealing film-Layer 4	Very low susceptibility to chloride concentrations (<10 mV in 10^{-2} to 10^{-6} M KCl range) and pH in the range of pH 3-11 (<2 mV), shelf life of more than 10 weeks, lifetime of more than several hours, drift rates of 0.28 to 0.55 mV/h.	Very low susceptibility to chloride (<10 mV in 10^{-2} to 10^{-6} M KCl range) and pH in the range of pH 3-11 (>2 mV), suitable for single and direct use	Disposable, not suitable for long term use	[71]
Printed PCB with infused Ag/AgCl and conductor-Layer 1 KCl in agar-Layer 2 PVC/CN or PVC/N membrane-Layer 3 Cellulose nitratre fixed with silicone-Layer 4	Drift rate of thin-film reference electrodes was about 0.2 mV/h for electrodes with a coating of PVC/CN and about 0.5 mV/h with PVC/N. The drift rate of thick- film electrodes was smaller (about 0.2 mV/h for electrodes with PVC/N and less than 0.1 mV for PVC/CN).	Very low drift rates (0.1-0.2 mV/h) suitable for long term use.	Depositing cellulose nitrate protective coating on top of a PVC membrane is difficult.	[20], [76]
Polyester flexible foil-Layer 1 Electrolyte layer (KCl)-Layer 2 Ag/AgCl internal electrode-Layer 3 Electrolyte layer (KCl)-Layer 4 Insulating paste-Layer 5	Drift rates of <0.2 mV/h, Lifetime of more than 10 days, shelf life of more than 9 months, almost no interference from Cl⁻, Br⁻, I⁻, CH_3COO^-, HPO_4^{2-}, $B_4O_7^{2-}$, TRIS*(HCl), EDTA, NH_3, $S_2O_3^{2-}$, H_2SO_4, ascorbic acid, $Cr_2O_7^{2-}$.	Simple structure with satisfactory shelf life (>9 months), almost no interference from Cl⁻, Br⁻, I⁻, CH_3COO^-, HPO_4^{2-}, $B_4O_7^{2-}$, TRIS*(HCl), EDTA, NH_3, $S_2O_3^{2-}$, H_2SO_4, ascorbic acid, $Cr_2O_7^{2-}$	Short lifetime (>9 months) for environmental applications	[22]
Ceramic substrate-Layer 1 Ag/AgCl-Layer 2 KCl doped hydrogel-Layer 3 Liquid junction membrane (PECVD silicon nitride)-Layer 4	Very fast hydration time of approximately 100 seconds and a stable potential for a lifetime of approximately 25-90 minutes, drift rates of 40-90 mV/h after the end of their life	Very fast hydration time (100 seconds) with stable potential (for 25-90 minutes) for disposable or short term applications	Very short lifetime (25-90 minutes) with very fast drift rates (40-90 mV/h), not for long term use.	[72]

Construction	Experimental results	Pros	Cons	Ref.
Alumina substrate-Layer 1 Silver conductor-Layer 2 Silver/silver chloride-Layer 3 KCl doped membrane made of dielectric paste D2020529D1 of GEM, the encapsulating resin EPOTEK H77 and a simple membrane made with polyisophthalamide diphenylsulfone (PIDS)-Layer 4	Best performances achieved with an encapsulating resin EPOTEK H77 and a PIDS membrane, stable potential with almost no drift for more than a month	Relatively long lifetime with no drift (>1 month)	In-house pastes and customized membranes making the electrode more expensive	[5]
Alumina substrate-Layer 1 Silver conductor-Layer 2 Silver/silver chloride-Layer 3 Agar gel with KCl-Layer 4 Chloroprene rubber-Layer 5	Insensitive to Na^+, K^+, Li^+, Ca^{2+}, NH^{4+}, and Cl^-, under continuous measurement conditions	High selectivity with low susceptibility (<15mV in the range of 1 to 10^{-6} M) to most important ionic species	Lifetime and shelf life of the electrodes was not fully investigated	[77]
PCB with a via hole-Layer 1 Copper/Silver-Layer 2 Copper/Silver/Silver Chloride-Layer 3 PVC membrane with ionic liquid ((1-dodecyl-3-methylimidazolium chloride)-Layer 4	Potential stability ±5 mV, high reproducibility and lifetime of more than 2 months	Moderate lifetime (>2 months) with promising potential stability, high reproducibility.	Higher price due to ionic liquids	[78]
Glass epoxy substrate-Layer 1 Conductive track-Layer 2 Ag/AgCl-Layer 3 Internal electrolyte layer-Layer 4 Insulating layer with two slits-Layer 5 Hydrophilic polymer-coated polyester film-Layer 6	Lifetime of approximately 60 minutes with very low susceptibility to chloride (<10 mV in the range of 10^{-3} to 1 M KCl)	Low chloride susceptibility (<10 mV in the range of 10^{-3} to 1 M KCl)	Complicated structural materials, short lifetime (60 minutes)	[73]
Alumina substrate-Layer 1 Silver conductor-Layer 2 Silver/silver chloride-Layer 3 Salt matrix (KCl) in polymeric paste (ESL 242SB)-Layer 4	Hydration period (1 h), lifetime (24 h), chloride susceptibility (10 mV/log[Cl^-]). As the thickness of the KCl matrix increases, the REs take longer to hydrate but exhibit longer lifetimes in a given range of chloride solutions (3.4 M to 0.0034 M). Furthermore, the RE's stability and response time is also influenced by the binder type used in the final salt reservoir layer.	Depending on the application, one can focus on longer lifetime with higher KCl percentages (>5%) but slower hydration times or vice versa		[46]
Alumina substrate-Layer 1 Silver conductor-Layer 2 Silver/silver chloride-Layer 3 Salt matrix (KCl) in hydrogel-Layer 4	Fast hydration (several minutes), lifetime (several days)	Direct use without the need to condition the electrode before use	Short lifetime (several days)unsuitable for long term use	[46]

Construction	Experimental results	Pros	Cons	Ref.
Polyamide substrate-Layer 1 Silver/silver chloride-Layer 2 Poly(dimethylsiloxane) (PDMS) liquid junction-Layer 3 PDMS electrolyte containing KCl-Layer 4 Protective layer-Layer 5	Lifetime of more than 2 months, immunity to Na^+, K^+, Cl^- and PO_4^{2-}, under continuous measurements	Relatively long lifetimes and very high selectivity with low susceptibilities to important ionic species	Complicated materials with increased cost	[40]
Alumina substrate-Layer 1 Silver conductor-Layer 2 Silver/silver chloride-Layer 3 Salt matrix (KCl) in polymeric paste (ESL 242SB)-Layer 4 Additional layer of (ESL 242SB)-Layer 5	Very low susceptibility to chloride of less than ±2 mV/pCl⁻ with lifetimes of more than several weeks, ±5 mV in a pH range of 3-10	Almost complete immunity to chloride concentration with relatively long lifetime, simple structure and materials	Not long enough lifetime for long term use of more than a year	[10], [70]
Alumina substrate-Layer 1 Silver conductor-Layer 2 Salt matrix (KCl) in polymeric paste (ESL 242SB)-Layer 3	Much lower chloride susceptibility (<10 mV/log [Cl⁻]) but higher drift rates (28.3 mV/day) and higher noise (N/A).	Very low susceptibility to chloride concentration (<10 mV/log [Cl⁻]) suitable for short term use.	Higher noise levels and faster drift rates (28.3 mV/day).	[12]
Water-repellent-treated paper substrate with a KCl-modified section-Layer 1 Ag/AgCl-Layer 2 Ag conductor-Layer3 Protective paste on both sides of the substrate-Layer 4	Hydration time of less than a minute, lifetime of up to 75 hours	Impressively fast hydration time suitable for instant use such as laboratorian applications or instant sample analysis, very low cost	Very short lifetime, unsuitable for any application requiring long term use	[74]
Substrate-Layer 1 Silver conductor-Layer 2 Silver/silver chloride-Layer 3 Photo-curable acrylic film containing immobilized sodium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB) and trimethylocthylammonium chloride (TOMA-Cl)-Layer 4	Low interference from several anions (>9 mV in a range of 10-8 to 10-1 M for Cl⁻, NO_3^-, Br⁻, SO_4^{2-}), high interference from perchlorate ion (173.2 mV in the same range of concentrations), short lifetime of about 5 hours.	Short lifetime (5 hours), suitable for laboratory use, huge interference from perchlorate ions.	High selectivity with low interference from other anions (>9 mV in a very wide concentration range)	[79]

4. Conclusions

The increasingly wide range of applications for ISEs and the ever increasing need for smart and intelligent systems raises an ever more urgent requirement for low-cost sensors. In particular, chemical, electrochemical and biosensors require a reliable and low-cost RE that will have comparable performance to that of the conventional liquid or gel-filled RE in terms of immunity to other ions and long term potential stability. There are numerous low-cost and miniaturised ISEs reported that are fabricated by several technologies but virtually every one of them is being tested and characterised against a conventional and highly-reliable liquid electrolyte Ag/AgCl RE. In applications where size, robustness, ruggedness and cost are of high importance, the use of the conventional Ag/AgCl RE is not suitable. Furthermore, attempts at simplifying, improving and miniaturising the ISEs are rendered meaningless without the existence of a similar low-cost, miniaturised and reliable RE.

Although there has been a significant amount of work done on potentiometric screen-printed sensors, knowledge regarding a reliable Ag/AgCl screen-printed RE is still only at a primal level. In this review paper, numerous attempts at the development of such a RE have been described, but none of these have exhibited comparable performance to the conventional liquid or gel-filled RE. As a general conclusion from the numerous attempts for the development of a screen-printed Ag/AgCl RE, the best fabrication procedure and pastes to be used are application specific. Currently, not a single Ag/AgCl reported has better or similar performances to its macroscale equivalent. Therefore, since some applications are more demanding with respect to long term stability and less concerned with hydration times or selectivity of the electrode, the electrode structure should be designed in such a way to meet the requirements of that specific application. In general, glass-based pastes have a much better adhesion on the substrate curing at much higher temperatures than polymers. That provides a much slower diffusion of KCl in the analyte but also increases the hydration time of the electrode. In applications were long term stability must be more than several hours and the hydration time is allowed to be large, a glass-based KCl salt matrix should be used with additional membranes, smaller contact areas, as large reservoirs as possible and longer channels. Furthermore, electrodes with glass-based inks have much higher impedances due to the much lower porosity of the layer compared to the polymer ones. In cases such as disposable electrodes, the hydration time needs to be very short while the long term stability is of lower importance. Usually, in these cases the selectivity of the electrodes becomes a more significant parameter. For this kind of application, polymer-based inks could be used and according to Glanc et al., the Ag/AgCl layer should be omitted as long as a top KCl matrix is deposited. In addition, hydrogels and high porosity membranes could be used with larger contact areas, shorter channels and smaller reservoir sizes should be used.

After the appearance of novel conducting polymers, ionic liquids and other carbon-based materials, the scientific community has tried to implement them for the development of a reliable screen-printed reference electrode not necessarily of the Ag/AgCl type. Although in the past, Ag/AgCl reference electrode seemed to be the most promising type of screen-printed reference electrodes, nowadays most scientists have moved to other directions such as ionophore-doped membranes using ionic liquids, nanomaterials [57], solid ion-conducting materials such as Nafion™ and more commonly, conducting polymers. Conducting polymers feature several advantages since they are in the solid form, can conduct electricity with very low currents and have low impedances, they are low-cost and they can be used as screen-printing inks. Furthermore, due to the fact that they are polymers, they can have high selectivity in terms of ions and substances and they can also have a long lifetime in aqueous solutions.

References

[1]   M. Sophocleous, 'Thick Film Underground Sensors', Southampton, 2016.

[2]   P. Y. Wee, 'The evaluation of thick film soil sensors for monitoring soil properties', University of Southampton, 2014.

[3]   M. Soleimani *et al.*, 'Engine oil acidity detection using solid state ion selective electrodes', *Tribol. Int.*, vol. 65, pp. 48–56, 2013.

[4]   A. Cranny, N. R. Harris, M. Nie, J. A. Wharton, R. J. K. Wood, and K. R. Stokes, 'Screen-printed potentiometric Ag/AgCl chloride sensors: Lifetime performance and their use in soil salt measurements', *Sensors Actuators, A Phys.*, vol. 169, no. 2, pp. 288–294, 2011.

[5]   R. Martinez-Manez *et al.*, 'A multisensors in thick-film technology for water quality control', *Sensors Actuators, A Phys.*, vol. 120, no. 2, pp. 589–595, 2005.

[6]   M. Prudenziati, 'The state of the art in thick film sensors', *Microelectronics J.*, vol. 23, pp. 133–141, 1992.

[7]   C. A. Galan-Vidal, J. Muniz, C. Dominguez, and S. Alegret, 'Chemical sensors, biosensors and thick-film technology', *Trends Anal. Chem.*, vol. 15, no. 5, pp. 225–231, 1995.

[8]   M. Haskard and K. Pitt, *Thick-Film Technology and Applications*. Electrochemical Publications, 1997.

[9]   M. A. Nolan, S. H. Tan, and S. P. Kounaves, 'Fabrication and characterization of a solid state reference electrode for electroanalysis of natural waters with ultramicroelectrodes', *Anal. Chem.*, vol. 69, pp. 1244–1247, 1997.

[10]   M. Glanc, M. Sophocleous, J. K. Atkinson, and E. Garcia-Breijo, 'The effect on performance of fabrication parameter variations of thick-film screen printed silver/silver chloride potentiometric reference electrodes', *Sensors Actuators, A Phys.*, vol. 197, pp. 1–8, 2013.

[11]   U. Guth, F. Gerlach, M. Decker, W. Oelßner, and W. Vonau, 'Solid-state reference electrodes for potentiometric sensors', *J. Solid State Electrochem.*, vol. 13, no. 1, pp. 27–39, 2009.

[12]   J. K. Atkinson, M. Glanc, M. Prakorbjanya, M. Sophocleous, R. Sion, and E. Garcia Breijo, 'Thick film screen printed environmental and chemical sensor array reference electrodes suitable for subterranean and subaqueous deployments', *Microelectron. Int.*, vol. 30, no. 2, pp. 92–98, 2013.

[13]   D. Ives and G. Janz, *Reference Electrodes: Theory and Practise*. Academic Press, 1961.

[14]   W. Vonau, W. Oelßner, U. Guth, and J. Henze, 'An all-solid-state reference electrode', *Sensors Actuators, B Chem.*, vol. 144, no. 2, pp. 368–373, 2010.

[15]   W.-J. Lan, E. J. Maxwell, C. Parolo, D. K. Bwambok, A. B. Subramaniam, and G. M. Whitesides, 'Paper-based electroanalytical devices with an integrated, stable reference electrode.', *Lab Chip*, vol. 13, no. 20, pp. 4103–4108, 2013.

[16]   M. Glanc-Gostkiewicz, M. Sophocleous, J. K. Atkinson, and E. Garcia-Breijo, 'Performance of miniaturised thick-film solid state pH sensors', *Sensors Actuators, A Phys.*, vol. 202, pp. 2–7, 2013.

[17]   D. Diamond, E. McEnroe, M. McCarrick, and A. Lewenstam, 'Evaluation of a new solid-state reference electrode junction material for ion-selective electrodes', *Electroanalysis*, vol. 6, no. 11–12, pp. 962–971, 1994.

[18]   I. Y. Huang and R. S. Huang, 'Fabrication and characterization of a new planar solid-state reference electrode for ISFET sensors', *Thin Solid Films*, vol. 406, no. 1–2, pp. 255–261, 2002.

[19]   I. Y. Huang, R. S. Huang, and L. H. Lo, 'Improvement of integrated Ag/AgCl thin-film electrodes by KCl-gel coating for ISFET applications', *Sensors Actuators, B Chem.*, vol. 94, no. 1, pp. 53–64, 2003.

[20]   A. Simonis, H. Lüth, J. Wang, and J. Schöning, 'Strategies of Miniaturised Reference Electrodes

Integrated in a Silicon Based "one chip" pH Sensor', *Sensors*, vol. 3, no. 9, pp. 330–339, 2003.

[21] J. Brignell, A. Cranny, and N. White, 'Sensor Applications of Thick-Film Technology', in *IEEE Proceedings on Solid-State & Electron Devices*, 1988.

[22] Ł. Tymecki, E. Zwierkowska, and R. Koncki, 'Screen-printed reference electrodes for potentiometric measurements', *Anal. Chim. Acta*, vol. 526, no. 1, pp. 3–11, 2004.

[23] A. E. Musa *et al.*, 'Disposable miniaturized screen-printed pH and reference electrodes for potentiometric systems', *Electroanalysis*, vol. 23, no. 1, pp. 115–121, 2011.

[24] O. Holmes and R. Loasby, *Handbook of Thick-Film Technology*. Electrochemical Publications, 1976.

[25] R. Belford, A. Owen, and R. Kelly, 'Thick-Film Hybrid pH Sensors', *Sensors and Actuators*, vol. 11, pp. 387–398, 1987.

[26] M. Prudenziati, 'Thick Film Technology', *Sensors Actuators, A Phys.*, vol. 25–27, pp. 227–234, 1991.

[27] C. Dumschat, M. Borchardt, C. Diekmann, and K. Cammann, 'Potentiometric Test Strip', *Sensors Actuators B Chem.*, vol. 24–25, pp. 279–291, 1995.

[28] A. Kisiel, H. Marcisz, A. Michalska, and K. Maksymiuk, 'All -solid-state reference electrodes based on conducting polymers', *Analyst*, vol. 130, pp. 1655–1662, 2005.

[29] S. M. Bidoki, D. M. Lewis, M. Clark, a Vakorov, P. a Millner, and D. McGorman, 'Ink-jet fabrication of electronic components', *J. Micromechanics Microengineering*, vol. 17, no. 5, pp. 967–974, 2007.

[30] A. Kisiel, A. Michalska, K. Maksymiuk, and E. A. H. Hall, 'All-Solid-State Reference Electrodes with Poly(n-butyl acrylate) Based Membranes', *Electroanalysis*, vol. 20, no. 3, pp. 318–323, 2008.

[31] W. Liao and T. Chou, 'Development of a Reference Electrode Chip for Application in Ion Sensor Arrays', *Z. Naturforsch*, vol. 63b, pp. 1327–1334, 2008.

[32] M. W. Shinwari, D. Zhitomirsky, I. A. Deen, P. R. Selvaganapathy, M. J. Deen, and D. Landheer, 'Microfabricated Reference Electrodes and thei Biosensing Applications', *Sensors2*, vol. 10, pp. 1679–1715, 2010.

[33] F. X. Rius-Ruiz, A. Kisiel, A. Michalska, K. Maksymiuk, and J. Riu, 'Solid-state reference electrodes based on carbon nanotubes and polyacrylate membranes', *Anal. Bioanal. Chem.*, vol. 399, pp. 3613–3622, 2011.

[34] A. Michalska, 'All-Solid-State Ion Selective and All-Solid-State Reference Electrodes', *Electroanalysis*, vol. 24, no. 6, pp. 1253–1265, 2012.

[35] W. Vonau, W. Oelßner, U. Guth, and J. Henze, 'An all-solid-state reference electrode', *Sensors Actuators B Chem.*, vol. 144, no. 2, pp. 368–373, 2010.

[36] J. C. B. Fernandes and E. V. Heinke, 'Alternative strategy for manufacturing of all-solid-state reference electrodes for potentiometry', *J. Sensors Sens. Syst.*, vol. 4, pp. 53–61, 2015.

[37] K. Eine, S. Kjelstrup, K. Nagy, and K. Syrverud, 'Towards a solid state reference electrode', *Sensors Actuators B Chem.*, vol. 44, pp. 381–388, 1997.

[38] M. Sophocleous, 'The investigation of Thick-Film Reference Electrodes', University of Southampton, 2009.

[39] G. Gritzner, *Handbook of Reference Electrodes*. 2013.

[40] I. Shitanda, H. Kiryu, and M. Itagaki, 'Improvement in the long-term stability of screen-printed planar type solid-state Ag/AgCl reference electrode by introducing poly(dimethylsiloxane) liquid junction',

Electrochim. Acta, vol. 58, no. 1, pp. 528–531, 2011.

[41]   L. Tymecki, S. Glab, and R. Koncki, 'Miniaturized, Planar Ion-selective Electrodes Fabricated by Means of Thick-film Technology', *Sensors*, vol. 6, no. 4, pp. 390–396, 2006.

[42]   J. Plambeck, *Electroanalytical Chemistry: Basic Principles and Applications*. United States of America: John Wiley & Sons, 1982.

[43]   C. Brett and A. Brett, *Electrochemistry: Principles, Methods and Applications*. Oxford: Oxford Science Publications, 1993.

[44]   A. Bard and L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Editio. United States of America: John Wiley & Sons, 2001.

[45]   A. W. J. Cranny and J. K. Atkinson, 'Thick film silver – silver chloride reference electrodes', *Meas. Sci. Technol.*, vol. 9, pp. 1557–1565, 1998.

[46]   J. K. Atkinson, M. Glanc, P. Boltryk, M. Sophocleous, and E. Garcia-Breijo, 'An investigation into the effect of fabrication parameter variation on the characteristics of screen printed thick film silver/silver chloride reference electrodes', *Microelectron. Int.*, vol. 28, no. 2, pp. 49–53, 2011.

[47]   D. Pletcher, *A first course in electrode processes*, 2nd Editio. Cambridge: The Royal Society of Chemistry, 2009.

[48]   F. Scholz, *Electroanalytical Methods: Guide to experiments and Application*, 2nd Editio. Berlin: Springer, 2010.

[49]   P. J. Lamas-Ardisana *et al.*, 'Disposable electrochemical paper-based devices fully fabricated by screen-printing technique', *Electrochem. commun.*, vol. 75, pp. 25–28, 2017.

[50]   F. Lisdat and W. Moritz, 'A reference element based on a solid-state structure', *Sensors Actuators B. Chem.*, vol. 15, no. 1–3, pp. 228–232, 1993.

[51]   C. Diekmann, C. Dumschat, K. Cammann, and M. Knoll, 'Disposable reference electrode', *Sensors Actuators B. Chem.*, vol. 24, no. 1–3, pp. 276–278, 1995.

[52]   J. J. Pedrotti, L. L. Angnes, and I. G. R. Gutz, 'Miniaturized reference electrodes with microporous polymer junctions', *Electroanalysis*, vol. 8, no. 7, pp. 673–675, 1996.

[53]   F. Yalcinkaya and E. T. Powner, 'Ag/AgCl/Cl- coated silver-stripe reference electrode', *Med. Eng. Phys.*, vol. 19, no. 3, pp. 299–301, 1997.

[54]   K. C. Honeychurch and J. P. Hart, 'Screen-printed electrochemical sensors for monitoring metal pollutants', *TrAC - Trends Anal. Chem.*, vol. 22, no. 7–8, pp. 456–469, 2003.

[55]   R. S. of Chemistry, 'Pseudo-reference electrode'. [Online]. Available: http://www.rsc.org/publishing/journals/prospect/ontology.asp?id=CMO:0002429&MSID=C1JM1098 7A.

[56]   H. Kaden and W. Vonau, 'Reference electrodes for electrochemical measurements', *J. Appl. Chem.*, vol. 340, no. 8, pp. 710–721, 1998.

[57]   P. Nicholas, R. Pittson, and J. P. Hart, 'Development of a simple, low cost chronoamperometric assay for fructose based on a commercial graphite-nanoparticle modified screen-printed carbon electrode.', *Food Chem.*, vol. 241, no. February 2017, pp. 122–126, 2017.

[58]   L. El Harrad and A. Amine, 'Amperometric biosensor based on prussian blue and nafion modified screen-printed electrode for screening of potential xanthine oxidase inhibitors from medicinal plants', *Enzyme Microb. Technol.*, vol. 85, pp. 57–63, 2016.

[59]   M. R. Majidi, Y. Omidi, P. Karami, and M. Johari-Ahar, 'Reusable potentiometric screen-printed sensor and label-free aptasensor with pseudo-reference electrode for determination of tryptophan in the presence of tyrosine', *Talanta*, vol. 150, pp. 425–433, 2016.

[60]   H. Shuai and Y. Lei, 'Graphene ink fabricated screen printed electrode for Cd2+ and Pd2+ determination in Xiangjiang river', *Int. J. Electrochem. Sci.*, vol. 11, no. 9, pp. 7430–7439, 2016.

[61]   E. K. Varadharajz and N. Jampana, 'Non-Invasive Potentiometric Sensor for Measurement of Blood Urea in Human Subjects Using Reverse Iontophoresis', *J. Electrochem. Soc.*, vol. 163, no. 7, pp. 340–347, 2016.

[62]   J. Y. Choi, K. Seo, S. R. Cho, J. R. Oh, S. H. K. Kahng, and J. Park, 'Screen-printed anodic stripping voltammetric sensor containing HgO for heavy metal analysis', *Anal. Chim. Acta*, vol. 443, no. 2, pp. 241–247, 2001.

[63]   S. Andreescu, T. Noguer, V. Magearu, and J. L. Marty, 'Screen-printed electrode based on ache for the detection of pesticides in presence of organic solvents', *Talanta*, vol. 57, no. 1, pp. 169–176, 2002.

[64]   W. Glasspool and J. Atkinson, 'A screen-printed amperometric dissolved oxygen sensor utilising an imobilised electrolyte gel and membrane', *Sensors Actuators B Chem.*, vol. 48, no. 1–3, pp. 308–3017, 1998.

[65]   W.-J. Guan, Y. Li, Y.-Q. Chen, X.-B. Zhang, and G.-Q. Hu, 'Glucose biosensor based on multi-wall carbon nanotubes and screen printed carbon electrodes.', *Biosens. Bioelectron.*, vol. 21, no. 3, pp. 508–512, 2005.

[66]   T. Tangkuaram, C. Ponchio, T. Kangkasomboon, P. Katikawong, and W. Veerasai, 'Design and development of a highly stable hydrogen peroxide biosensor on screen printed carbon electrode based on horseradish peroxidase bound with gold nanoparticles in the matrix of chitosan', *Biosens. Bioelectron.*, vol. 22, no. 9–10, pp. 2071–2078, 2007.

[67]   S. Carrara, V. V. Shumyantseva, A. I. Archakov, and B. Samorì, 'Screen-printed electrodes based on carbon nanotubes and cytochrome P450scc for highly sensitive cholesterol biosensors', *Biosens. Bioelectron.*, vol. 24, no. 1, pp. 148–150, 2008.

[68]   U. B. Trivedi *et al.*, 'Potentiometric biosensor for urea determination in milk', *Sensors Actuators, B Chem.*, vol. 140, no. 1, pp. 260–266, 2009.

[69]   J. Prasek, M. Adamek, J. Krivka, and I. Szendiuch, 'Reference electrodes for thick-film sensors', *2008 31st Int. Spring Semin. Electron. Technol. Reliab. Life-time Predict. ISSE 2008*, pp. 514–517, 2008.

[70]   M. Sophocleous, M. Glanc-Gostkiewicz, J. K. Atkinson, and E. Garcia-Breijo, 'An experimental analysis of Thick-Film solid-state reference electrodes', in *IEEE Sensors Conference*, 2012.

[71]   A. Mroz, M. Borchardt, C. Diekmann, K. Cammann, M. Knoll, and C. Dumschat, 'Disposable reference electrode', *Analyst*, vol. 123, pp. 1373–1376, Mar. 1998.

[72]   J. Ha *et al.*, 'A polymeric junction membrane for solid-state reference electrodes', *Anal. Chim. Acta*, vol. 549, no. 1–2, pp. 59–66, 2005.

[73]   K. Idegami, M. Chikae, N. Nagatani, E. Tamiya, and Y. Takamura, 'Fabrication and characterization of planar screen-printed Ag/AgCl reference electrode for disposable sensor strip', *Jpn. J. Appl. Phys.*, vol. 49, no. 9 PART 1, 2010.

[74]   I. Shitanda, M. Komoda, Y. Hoshi, and M. Itagaki, 'An instantly usable paper-based screen-printed solid-state KCl/Ag/AgCl reference electrode with long-term stability', pp. 6481–6484, 2015.

[75]   D. Desmond, B. Lane, J. Alderman, J. . Glennon, Dermot Diamond, and D. W. . Arrigan, 'Evaluation of

miniaturised solid state reference electrodes on a silicon based component', *Sensors Actuators B Chem.*, vol. 44, no. 1–3, pp. 389–396, 1997.

[76]   A. Simonis *et al.*, 'New concepts of miniturised reference electrodes in silicon technology for potentiometric sensor systems', *Sensors Actuators B Chem.*, vol. 103, no. 1–2, pp. 429–435, 2004.

[77]   W. Liao and T. Chou, 'Fabrication of a Planar-Form Screen-Printed Solid Electrolyte Modified Ag / AgCl Reference Electrode for Application in a Potentiometric Biosensor Fabrication of a Planar-Form Screen-Printed Solid Electrolyte Modified Ag / AgCl Reference Electrode for App', *Anal. Chem.*, vol. 78, no. 12, pp. 4219–4223, 2006.

[78]   R. Mamińska, A. Dybko, and W. Wróblewski, 'All-solid-state miniaturised planar reference electrodes based on ionic liquids', *Sensors Actuators, B Chem.*, vol. 115, no. 1, pp. 552–557, 2006.

[79]   S. Alva, L. Y. Heng, and M. Ahmad, 'Optimization of Screen Printed Reference Electrode Based on Charge Balance and Poly (Butyl Acrylate) Photocurable Mebrane', *Int. J. Innov. Mech. Eng. Adv. Mater. (IJIMEAM)*, vol. 2, no. 1, pp. 10–15, 2016.