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Screen-printed potentiometric Ag/AgCl chloride sensors: Lifetime performance and their use in soil salt measurements

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ABSTRACT

Silver–silver chloride electrodes (Ag/AgCl) for the detection of chloride ions were fabricated using thick-film technology. Five different formulations were prepared and chloride responses were investigated over time. Almost identical and near Nernstian responses were observed over the first 162 days with an average chloride sensitivity for all formulations of −51.12 ± 0.45 mV per decade change in chloride concentration compared with a value of −50.59 ± 0.01 mV over 388 days for the best two formulations. After 6-months continuous immersion in tap water, pastes formulated with a glass binder began to exhibit a loss in sensitivity whilst those formulated from a commercial thick-film dielectric paste remained functional for the best part of a year. This difference in lifetime performance is attributed to the inclusion of proprietary additives in the commercial paste aiding adhesion and minimising AgCl leaching. The mechanical and chemical robustness of these electrodes has been demonstrated through their ability to detect changing levels of chloride when immersed in soil columns. This particular capacity will make them an invaluable tool in the fields of hydrology, agricultural science, soil science and environmental science.

1. Introduction

As well as being the functional component of the Ag/AgCl reference electrode used ubiquitously in electrochemical measurements, the chloride sensor has an important role in many other application areas. It may be argued that its conventional fabrication through the chloridisation of a silver wire is a relatively simple process, but without appropriate packaging such devices are inherently fragile. Whilst this may not be a problem in laboratory based measurements, this form of sensor does restrict its use in many real world applications. For example, our group are concerned with the development of electrochemical sensors to detect products of corrosion and to monitor in situ the evolving chemical processes that occur during corrosion in marine and aerospace structures. Chloride has an important role in many corrosion processes (*e.g.* in the formation of protective oxide films on copper-based alloys in the marine environment [1] and as an indicator of the occurrence of crevice corrosion [2]) and so its detection is of interest. However, considering that the sensor might be exposed to harsh environments or located at installations that are mechanically challenging, its use in this area would be beyond the capabilities of a simple wire electrode.

A further application area in which we are interested is the monitoring of salt levels within soil, particularly in regions where, for example, rising ground water levels are bringing salt to the soil surface and destroying what was once arable farming land. The development of a probe instrument that can be inserted into the ground to directly measure chloride levels as a function of immersion depth would be a boon, but again necessitates that the sensor be rugged in construction. Clearly in these situations there is a requirement for a more robust implementation of the chloride sensor. Screen printing sensors using thick-film technology offers this possibility.

2. Theory

In its simplest form, the Ag/AgCl electrode consists of a silver wire that is coated with a layer of silver chloride. It is essentially an ion-selective electrode that exhibits a strong sensitivity to chloride ion activity. The electrochemical reaction occurring at the electrode is given by:

$$AgCl_{(s)} + e^{-} \leftrightarrow Ag_{(s)} + Cl_{(aq)}{}^{-} \qquad (1)$$

The steady state or equilibrium potential (E) associated with this reaction is related to the activities of the reactant and dissociation

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Table 1
Printing screen parameters used for test structures.

Layer	Paste	Mesh density (lpi)[a]	Mesh opening (μm)	Wire diameter (μm)	Open area (%)	Emulsion thickness (μm)
Ag	ESL 9912-A	325	50	30	39	15
AgPd	ESL 9635	325	50	30	39	25
Insulator	ESL 4905-CH	325	50	30	39	25
AgCl	See Table 2	200	90	40	48	25

[a] Traditionally, screen mesh densities are expressed in lines per inch (lpi).

products and can be expressed by the Nernst equation [3,4]:

$$E = E^{\theta\prime} + \left(\frac{RT}{nF}\right) \ln \left[\frac{a_{\mathrm{AgCl}}}{a_{\mathrm{Ag}} a_{\mathrm{Cl}^-}}\right] \qquad (2)$$

where $E^{\theta\prime}$, the electrode formal potential (V); R, the molar gas constant (8.31 J K^{-1} mol^{-1}); T, the absolute temperature (K); n, the stoichiometric number of electrons transferred in the reaction ($n = 1$); F, the Faraday constant (96485 C mol^{-1}); a_{x}, the activity of species x.

The activity of an ionic species is equal to the product of its concentration and its activity coefficient. Noting that the activity coefficient for chemical species in the solid phase is defined as unity and recognizing that at low to moderate chloride ion concentrations the chloride ion activity coefficient is also approximately unity [5,6], Eq. (2) may be expressed in terms of concentrations rather than activities, thus:

$$E = E^{\theta\prime} + \left(\frac{RT}{nF}\right) \ln \left[\frac{|\mathrm{AgCl}|}{|\mathrm{AgCl}| \cdot |\mathrm{Cl}^-|}\right] \qquad (3)$$

Because silver chloride is a sparingly soluble salt, its concentration should ideally remain constant in aqueous media. Likewise, the concentration of silver should also remain constant since it is in a solid phase. Hence, the ratio of the concentrations of silver chloride to silver, k, should remain constant and Eq. (3) may be rewritten as:

$$E = E^{\theta\prime} + \left(\frac{RT}{nF}\right) \ln \left[\frac{k}{|\mathrm{Cl}^-|}\right] \qquad (4)$$

By inverting and separating the logarithmic term and then converting to base 10 yields:

$$E = E^{\theta\prime} - 2.303 \left(\frac{RT}{nF}\right) \cdot [\log |\mathrm{Cl}^-| - \log(k)] \qquad (5)$$

Substituting for the various constants at a temperature of 25 °C yields:

$$E = E^{\theta\prime} - 0.0592 \log |\mathrm{Cl}^-| + 0.0592 \log(k) \qquad (6)$$

Hence, under ideal conditions and at an operating temperature of 25 °C, the measured electrode potential (E) theoretically decreases by approximately 59 mV for every decade change in chloride ion concentration. Eq. (6) however also reveals that for any given chloride concentration, the measured potential can change if the ratio (k) of silver chloride to silver changes.

3. Sensor fabrication

The chloride sensors were fabricated using standard thick-film processing techniques where structures are built up by the sequential printing and appropriate curing of a number of layers of different functional materials in the form of printable pastes [7,8]. Printing was performed using a state-of-the-art DEK 248 screen printer incorporating vision assisted alignment. The printing process involves the deposition of the pastes through emulsion covered stainless steel mesh screens where open areas that define the shape to be printed have been patterned in the screen emulsion by photolithography. The pastes are drawn through the patterned areas of the screen by surface tension onto a substrate located at a set distance beneath the screen as the screen is deflected downward by the passage of a rubber squeegee across its surface. Both the speed of the squeegee and the pressure it exerts onto the screen are user controlled. The screen mesh density and mesh filament diameter define the minimum feature size that can be printed and in conjunction with the emulsion thickness, squeegee pressure and speed, control the print thickness. Appropriate screen parameters were selected to suit the different rheologies of the various pastes used in the fabrication of the sensors (see Table 1).

Fig. 1 shows a schematic of the various layers that comprised a single chloride sensor test structure. First, a strip of a commercial thick-film silver paste (Electro Science Laboratories (ESL), 9912-A) was printed upon laser scribed 96% alumina substrate (Hybrid Laser Tech) to form the electrode back contact. At one end of the silver strip, a small region of silver–palladium paste (ESL, 9635) was printed over the silver layer to produce a solderable electrical connection. A glass dielectric paste (ESL, 4905CH) was then printed over the majority of the silver electrode length to serve as an insulation layer, leaving the terminal end free and a window at the other end to define the active electrode area. Finally, one of the several proprietary Ag/AgCl pastes was printed over the windowed area at the active end of the electrode structure.

After printing each layer, the test structure was dried in a 4-zone belt furnace with a peak temperature of 150 °C with a 15 min cycle (BTU DR92-5-60D conveyor furnace). Each layer was then thermally cured with a temperature profile suitable for the material being processed. In the case of the commercial pastes (the silver, silver–palladium and insulating dielectric composition), this was performed in an 8-zone belt furnace (BTU TFF92-8-90A24GT fast fire conveyor furnace) with peak temperature of 850 °C, temperature ascent and descent rates of 50 °C/min and a total cycle length of 1 h. By comparison, because silver chloride has a melting point of 457 °C, the proprietary Ag/AgCl pastes were cured in a box oven at various lower temperatures as detailed in Table 2.

The proprietary Ag/AgCl pastes were produced by mixing biosensor grade silver chloride powder of an average particle size of 10 μm (MCA Services, BGSC(ST)-2) and silver powder (Sigma–Aldrich, purity >99.9%, 2–3.5 μm particle size) into either

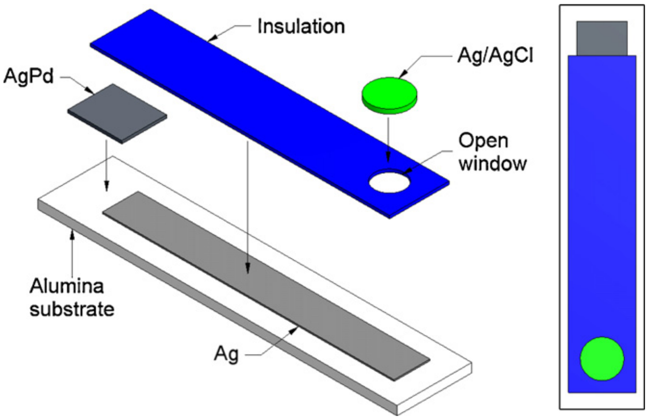

Fig. 1. Schematic diagram of a single Ag/AgCl electrode.