

Lifetime performance characteristics of screen-printed potentiometric Ag/AgCl chloride sensors

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Abstract: Ag/AgCl chloride sensors were fabricated using thick-film technology. A number of different formulations were prepared and chloride responses were investigated over time. Near Nernstian, identical responses were observed over the first 160 days with an average chloride sensitivity of -51.8 ± 0.4 mV per decade change in chloride concentration (pCl), irrespective of paste formulation. 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. The difference is attributed to the inclusion of proprietary additives in the commercial paste aiding adhesion and minimising AgCl leaching.

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 such as the measurement of salinity. Whilst it may be argued that its conventional fabrication through the chloridisation of a silver wire is a relatively straightforward process, without appropriate packaging such devices are inherently fragile. There is no doubt that there is a market for a more robust, cheap, mass produced, disposable alternative. Thick-film technology offers this possibility.

The chloride sensors were fabricated in a planar configuration and comprise a proprietary Ag/AgCl layer deposited over a printed silver back contact (ElectroScience Laboratories (ESL), 9912-A) upon an inert 96% alumina substrate (Coors Ceramics, ADS-96R) as shown in Fig. 1. A glass

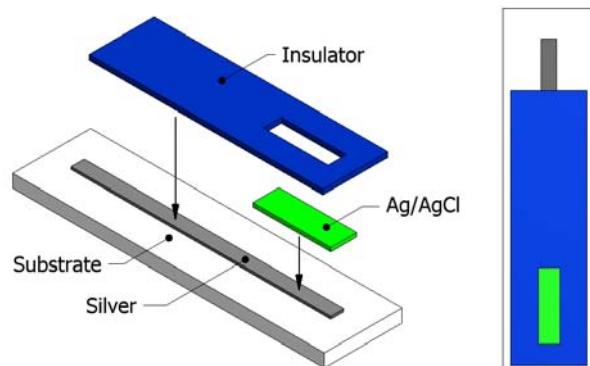


Fig. 1. Schematic of a single Ag/AgCl electrode.

dielectric paste (ESL, 4905CH) was then printed over the majority of the silver electrode length as an insulation layer, leaving one end free as a solderable terminal and a patterned window at the other end defining the active electrode area (4.0 mm x 2.0 mm).

Proprietary Ag/AgCl pastes were produced by mixing biosensor grade silver chloride powder (MCA Services, BGSC(ST)-2) and silver powder (Sigma Aldrich, purity >99.9%, 2-3.5 μ m particle size) with either a lead borosilicate glass (Ferroperm, CF7575) or commercial thick-film dielectric paste (ESL, 4026). Five different formulations for the Ag/AgCl paste were prepared representing the 2 different glass binders, 4 different stoichiometries of the silver to silver chloride to glass binder ratio and 3 different firing profiles as summarised in Table 1. Each paste was rendered into a suitable consistency for screen printing by mixing with an organic vehicle (ESL, 401) and dispersing with a stainless steel triple-roll mill.

2 Results: Electrode performance was assessed by potentiometric measurement with respect to an Ag/AgCl (3.5M KCl) reference electrode (VWR, GelPlas) over nearly 4 decades of chloride concentration

Table 1: Composition and firing profiles of different Ag/AgCl pastes used as test structures.

| Sample | Stoichiometry | Glass | Firing Profile |
|--------|-------------------------------|------------------|---------------------------------|
| # 1 | 20% Glass : 53% AgCl : 27% Ag | Ferroperm CF7575 | 475°C, 80 mins. |
| # 2 | 30% Glass : 47% AgCl : 23% Ag | Ferroperm CF7575 | 425°C, 80 mins. |
| # 3 | 40% Glass : 40% AgCl : 20% Ag | Ferroperm CF7575 | 425°C, 80 mins. |
| # 4 | 50% Glass : 33% AgCl : 16% Ag | ESL 4026 | 475°C, 80 mins. |
| # 5 | 50% Glass : 33% AgCl : 16% Ag | ESL 4026 | 350°C, 30 mins, 475°C, 30 mins. |

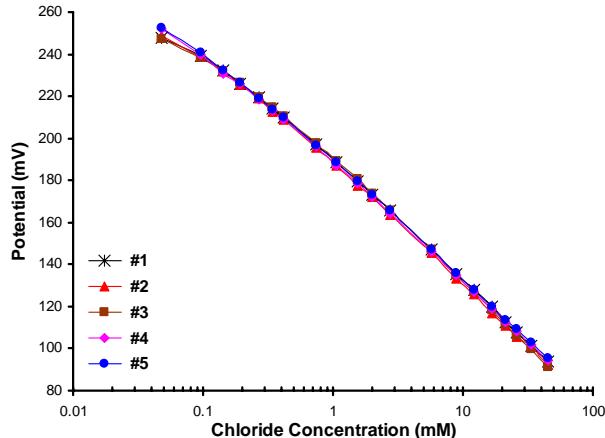


Fig 2. Chloride response on ninth day.

in the form of potassium chloride (Fluka, Ultra >99.5%) using a Keithley model 2000 digital multimeter (input impedance $> 10^{10}$ Ohms). Between measurements, the electrodes were intentionally stored in tap water as an example of a non-ideal environment. A typical response obtained after just one week continuous immersion is shown in Fig. 2, where attention is drawn to the fact that the x-axis has a logarithmic scale. The figure shows that all five sample devices have very similar responses and demonstrate linear relationships between potential and chloride concentration.

Fig. 3 shows the chloride sensitivity expressed as mV per decade change in concentration (mV/pCl) for all 5 samples over a 334-day period, including the average response with $\pm 5\%$ limit bands. This shows that following a short period of hydration (1 day) all 5 sensors exhibit a chloride sensitivity that remains within $\pm 5\%$ of an average value of -51.8 ± 0.4 mV /pCl for approximately 160 days. After this time, devices #1 and #2 begin to lose sensitivity followed by device #3 at around 300 days. All three of these devices share a common glass binder, with the highest loading being for device #3.

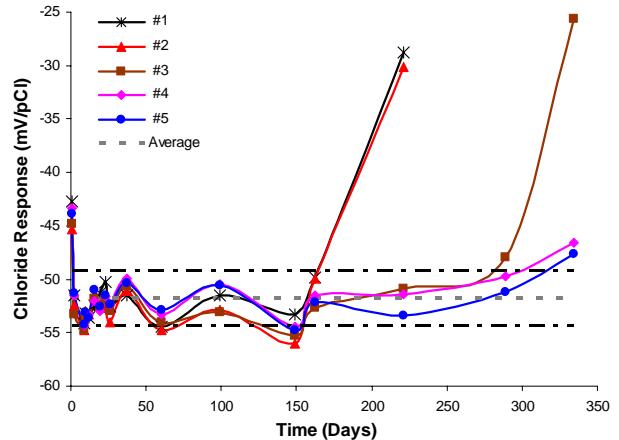


Fig 3. Chloride response over 334-days.

Loss in sensitivity is attributed to the differences in the adhesive qualities of the two glass binders and their abilities to bind the constituent components of the Ag/AgCl pastes together, with the commercial paste understandably demonstrating superiority; having been developed specifically as a thick-film compatible material.

3 Conclusions: Screen-printed Ag/AgCl electrodes demonstrate near Nernstian responses to chloride concentration in the range investigated covering 0.05 to 50 mM. Lifetimes in excess of 150 days have been demonstrated which is adequate for many applications where a cheap chloride sensor is required, e.g. soil salinity measurements. Results suggest that it does not matter what loading of AgCl is used to achieve a chloride response. An additional challenge is to find a suitable method of using these electrodes in the pursuit of a low-cost, solid-state, true reference electrode [1].

Acknowledgements

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References

[1] A. Cranny and J.K. Atkinson, "Thick film silver-silver chloride reference electrodes", Meas. Sci. and Tech., vol. 9, pp. 1557-1565, 1988.