Screen-Printed Potentiometric Chloride Sensors

Andy Cranny, Nick Harris and Neil White

School of Electronics and Computer Science, University of Southampton, Hampshire, SO17 1BJ, UK

Tel: +44 23-8059-9204 Fax: +44 23-8059-2931 Email: awc@ecs.soton.ac.uk

Introduction

Chloride sensors have use in many agronomical and environmental applications, for example:

- Measurement of soil salinity;
- Identification of hydrological pathways through water catchment areas;
- Irrigation management using saline sources;
- Water quality management and regulation.

A potentiometric chloride sensor is formed when a layer of silver chloride (AgCl) is grown on a silver electrode. The resulting structure generates a potential that has a logarithmic response to chloride ion concentration. The response is governed by the Nernst equation which predicts a sensitivity of approximately -59.2 mV per decade change in chloride concentration (pCl) at a temperature of 298 K, and is given by:

$$E = E_o - 0.0592 \log C_{Cl^-}$$

Here, E = Electrode potential (V)
E_o = Offset potential (V)
C_{Cl^-} = Chloride ion concentration (M)

Sensor Fabrication

Chloride sensors were made using screen printing pastes obtained from ElectroScience Laboratories. First, a glassy silver electrode (ESL 9912-A) is printed onto an alumina tile, as shown in Figure 1. This is over-printed with a waterproof glass layer (ESL 4905CH) that defines the active area of the sensor and leaves a solderable terminal end.

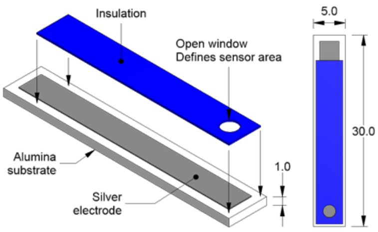

Figure 1: Schematic of screen printed chloride sensor (dimensions in mm).

Two methods were investigated to electrochemically grow the AgCl layer:

- Amperostatic coulometry (controlled current)
- Asymmetric square wave voltammetry, aSWV (controlled voltage)

In the amperostatic technique, AgCl is grown on the exposed electrode surface by passing an electric current. The amount of AgCl grown is directly proportional to the total charge supplied to the electrode. In this study AgCl was grown in 1 M solutions of potassium chloride (KCl), hydrochloric acid (HCl), calcium chloride ($CaCl_2$) or ferric chloride ($FeCl_3$), and at different charge densities.

In the second technique, a cyclical asymmetric square wave potential is applied to the electrode a number of times. When the potential is positive, AgCl grows on the electrode surface; when negative, it is stripped away. To ensure net growth of an AgCl layer, asymmetry is included in the waveform, either by differences in the magnitudes of the growth and stripping potentials (Vg and Vs) or by differences in the times that these potentials are applied (Tg and Ts), as shown in Figure 2.

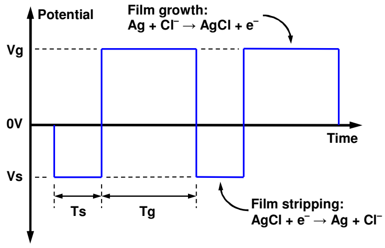

Figure 2: Generic form of asymmetric chloridising waveform (2 cycles shown).

Sensor Characterisation

Sensor calibration was performed by measuring their potentials with respect to a Ag/AgCl reference electrode (3.5 M KCl) in deionised water, to which controlled volumes of 10 mM, 100 mM or 1 M KCl were added at 15 minute intervals: resulting chloride concentrations were determined empirically. A typical set of calibration data is shown in Figure 3. The insert gives an indication of how quickly the sensors reach a stable response.

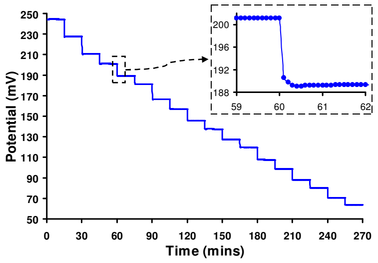

Figure 3: Typical sensor response measured during calibration trials.

Results

Average responses (n = 4) of chloride sensors produced by amperostatic coulometry are shown in Figure 4 (as a function of charge density) and in Figure 5 (as a function of chloridising ion source). All sensor types exhibit good logarithmic responses to chloride concentration, with no obvious differences attributable to production parameters.

Chloride sensitivity values and calibration offset potentials were calculated from the data and are summarised in Table 1.

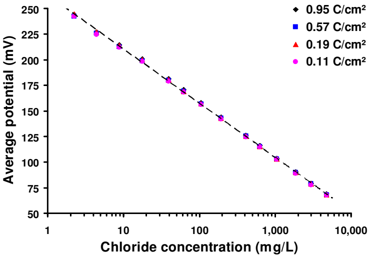

Figure 4: Average responses for sensors produced by coulometry, as a function of charge density. Broken line = best logarithmic fit.

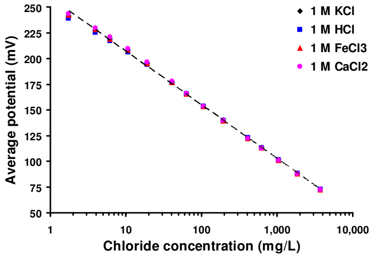

Figure 5: Average responses for sensors produced by coulometry, as a function of ion source. Broken line = best logarithmic fit.

Chloride source	Charge density (*C/cm²*)	Sensitivity (*mV/pCl*)	Offset (*mV*)
KCl	0.11	-52.6 ± 0.4	22.3 ± 0.6
KCl	0.19	-53.1 ± 0.1	22.2 ± 0.2
KCl	0.57	-52.5 ± 0.3	23.2 ± 0.4
KCl	0.95	-53.0 ± 1.5	23.1 ± 2.4

Chloride source	Charge density (*C/cm²*)	Sensitivity (*mV/pCl*)	Offset (*mV*)
KCl	3.0	-52.0 ± 0.1	22.6 ± 1.5
HCl	3.0	-51.3 ± 1.3	23.6 ± 1.9
$CaCl_2$	3.0	-53.0 ± 1.7	20.4 ± 3.3
$FeCl_3$	3.0	-52.4 ± 0.8	21.4 ± 1.7

Table 1. Average response parameters for chloride sensors produced by amperostatic coulometry.

Average responses (n = 3) for chloride sensors produced by aSWV are shown in Figure 6 (as a function of stripping potential, Vs) and in Figure 7 (as a function of AgCl growth to stripping time ratio, Tg:Ts). All sensor types exhibit good logarithmic responses to chloride concentration, with no obvious differences attributable to production parameters.

Table 2 summarises the chloride sensitivity values and calibration offset potentials calculated from the data for these sensors.

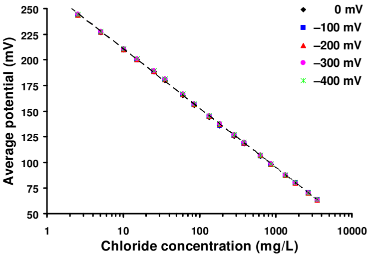

Figure 6: Average responses for sensors produced by aSWV, as a function of stripping potential. Broken line = best logarithmic fit.

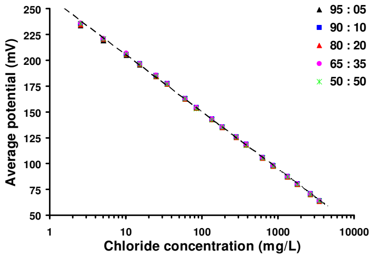

Figure 7: Average responses for sensors produced by aSWV as a function of time ratio, Tg:Ts. Broken line = best logarithmic fit.

Tg:Ts (%)	Vg (mV)	Vs (*mV*)	Sensitivity (*mV/pCl*)	Offset (*mV*)
50 : 50	+400	-400	-57.9 ± 0.1	5.7 ± 0.1
50 : 50	+400	-300	-57.9 ± 0.1	5.6 ± 0.2
50 : 50	+400	-200	-57.7 ± 0.2	5.7 ± 0.2
50 : 50	+400	-100	-57.7 ± 0.3	5.3 ± 0.2
50 : 50	+400	0	-57.7 ± 0.1	5.1 ± 0.8

Tg:Ts (%)	Vg (mV)	Vs (*mV*)	Sensitivity (*mV/pCl*)	Offset (*mV*)
95 : 05	+400	-400	-54.9 ± 0.2	9.9 ± 0.2
90 : 10	+400	-400	-55.2 ± 0.3	9.3 ± 0.3
80 : 20	+400	-400	-53.3 ± 0.2	8.8 ± 0.3
65 : 35	+400	-400	-55.5 ± 0.1	8.9 ± 0.3
50 : 50	+400	-400	-55.4 ± 0.1	8.7 ± 1.5

Table 2. Average response parameters for chloride sensors produced by aSWV.

Conclusions

- Potentiometric sensors with electrochemically grown AgCl films produce near Nernstian response to chloride over a large concentration range.
- No significant differences are observed in their response characteristics as a function of the film growth method.
- In general, larger values for chloride sensitivity and lower calibration offset values, both with narrower spread, were observed with sensors fabricated using aSWV. This may be due to the cyclical process of film growth and stripping producing higher purity films of AgCl, since electroactive impurities are also proportionately removed.

Acknowledgements

This work was funded by the UK's Biotechnology and Biological Sciences Research Council (BBSRC), grant number BB/J021210/1.

Eurosensors XXVIII, 7-10 September 2014, Brescia, Italy