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## Screen Printed Potentiometric Chloride Sensors

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### Abstract

Potentiometric chloride sensors were fabricated by electrochemically chloridizing the surface of screen printed silver electrodes using amperostatic coulometry or asymmetric square wave voltammetry. In the case of coulometric chloridization, the effect of different chloride ion sources was also investigated. The response to chloride ions by each type of sensor was determined by measuring their potentials with respect to a commercial Ag/AgCl reference electrode over the chloride concentration range 1.8 to 3,545 mg/L (approximately 50  $\mu$ M to 100 mM). Results reveal that irrespective of fabrication method, all sensors exhibit near Nernstian responses with no significant relationships between fabrication and response parameters.

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### 1. Introduction

There is a need for chloride sensors for application in agronomical and environmental studies. For example, a chloride sensor would be an invaluable tool for hydrology since it offers a direct and simple method to track and map the flow of water through terrains. Moreover, selective and considered spatial distribution of chloride sensors will enable quantitative measures of the chloride retention capacity of different terrains and soil types; a useful tool for soil scientists. Furthermore, a chloride sensor gives a qualitative measure of soil salinity; a particularly important indicator for agricultural management. On larger scales, field wide deployments of networks of sensors would give an unprecedented insight into how soil conditions vary over time and growing seasons, and such applications are becoming more viable with the advent of wireless sensor networks. Potential applications that could be enabled

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would be precision fertilizer applications, precision irrigation and control of salinity of environments. The significant hurdle in realizing these applications is the lack of suitable sensors which preferably need to be robust, low cost and low maintenance. Commercial chloride sensors typically utilize ion-selective membranes which are inherently fragile and can be costly. Screen printing offers a cheap and viable route for the production of chloride sensors. We have previously reported on screen printed potentiometric chloride sensors fabricated using proprietary printable AgCl as the sensing layer [1] and demonstrated their suitability for measuring chloride content in soils [2]. In this paper we turn our attention to the formation of the sensing layer by different electrochemical methods.

## 2. Sensor fabrication

Potentiometric chloride sensors were produced by electrochemically growing silver chloride (AgCl) over the surface of silver electrodes. When immersed in solution, this ion-sensitive electrode generates a potential dependant on the relative proportions of Ag, AgCl and chloride ions present at the interface with the solution. Ideally the electrode potential should exhibit a logarithmic relationship with the chloride concentration in accordance with the Nernst equation, which predicts that at a temperature of 298 K, the electrode potential decreases by -59.2 mV for each decade change in chloride concentration (pCl). In this study AgCl was grown on screen printed Ag electrodes in 1 M potassium chloride (KCl) solution by amperostatic coulometry or by asymmetric square wave voltammetry (aSWV) using an Autolab PGSTAT302N potentiostat. Fig. 1 illustrates the basic electrode structure used. Details of its fabrication and operating theory can be found in our previous publications [1, 2].

In the amperostatic technique (constant current), AgCl is grown on the exposed electrode surface by passing a current through the electrode. The amount of AgCl grown is directly proportional to the total charge supplied to the electrode (cf. Faraday's Law), which in turn is defined by the product of the current magnitude and the time it is applied. In this study AgCl was grown on the surfaces of electrodes with diameters of 2.0 mm or 2.6 mm, by applying currents of either 0.2 mA or 1.0 mA for 2 minutes. Because different combinations of electrode area and current were used, the resultant sensors were categorized by charge density, wherein large values imply thicker deposits of AgCl per unit electrode surface area. In a separate experiment, the effects of the chloridizing ion source were investigated by chloridizing separate groups of 4 identical silver electrodes in 1 M solutions of either potassium chloride (KCl), hydrochloric acid (HCl), calcium chloride (CaCl<sub>2</sub>) or ferric chloride (FeCl<sub>3</sub>).

In the aSWV technique (constant voltage) a cyclical asymmetric square wave potential is applied to the electrode a number of times. When the waveform potential is positive, AgCl grows on the electrode surface; when negative, it is stripped from the electrode surface. To ensure net growth of AgCl, asymmetry is included in the potential waveform, either by differences in the magnitudes of the plating and stripping potentials or by differences in the times that these potentials are applied (duty cycle). By growing a film in a continuous cycle of plating and stripping it is expected that a more homogenous film will be produced since the weakest bound molecules of AgCl will be the first removed during the stripping process. To set appropriate potentials to grow and strip AgCl, cyclic voltammetry was performed on a silver electrode in a 1 M KCl solution to determine the potential ranges over which these processes occurred. Fig. 2 shows results from cyclic voltammetry performed on an Ag electrode in 1 M KCl solution where the potential was scanned between potential limits of  $\pm 800$  mV at a rate of 20 mV/s with step size of 5 mV in the direction shown by the numbered arrows. Observation of the electrode surface during this experiment revealed that AgCl grew at positive potentials in excess of +50 mV and was stripped at negative potentials below -25 mV.

In this study, sensors were produced using two different forms of aSWV: asymmetry in time and asymmetry in potential levels. In the first category, 5 groups of 3 identical Ag electrodes were chloridized using a square wave signal with equal potentials for film growth and stripping (+400 mV and -400 mV, respectively) and of 10 s period, but with different ratios for the length of times these potentials were applied, ranging from 95% down to 50% in favor of film growth. The square wave signal was cycled a number of times, with the number of cycles being dependant on the length of the film growth period, such that the product of these two parameters was constant for all sensor types formed by this method. In the second category, a further 5 groups of 3 identical electrodes were chloridized with 120 cycles of a potential waveform with equal period for the film growth and stripping phases (5 s each), a +400 mV potential value for the growth phase, but with different potential values for the stripping phase ranging from 0 mV down to -400 mV.

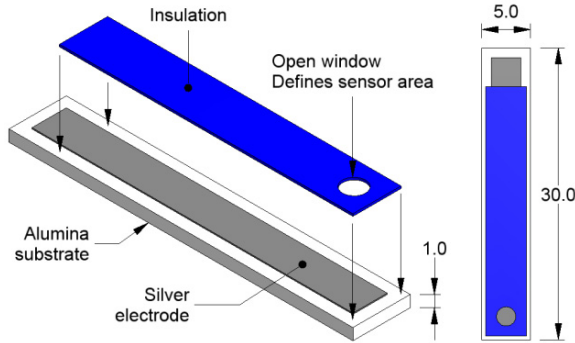


Fig. 1: Schematic of screen printed electrode (dimensions in mm).

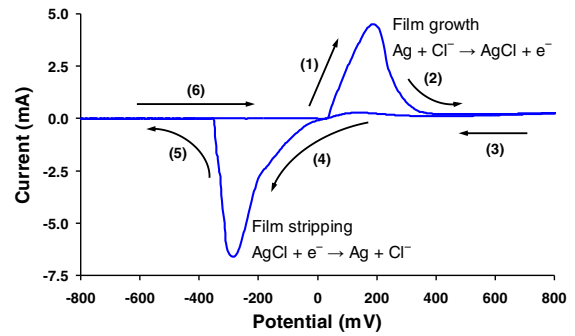


Fig. 2: Cyclic voltammogram for Ag electrode in 1 M KCl.

### 3. Sensor response

The response of the various types of sensor to chloride ions was evaluated by measuring their potentials with respect to a commercial Ag/AgCl reference electrode (VWR GelPlas, 3.5 M KCl) using a National Instruments 6015 DAQPad data acquisition system controlled by bespoke software implemented using LabVIEW. Up to 16 sensors are connected to the measurement system and potentials from each are measured at a rate of 1 kHz. At 6 second intervals, the most current 100 readings from each sensor are averaged before being written to a data storage file. Chloride levels were varied by adding known volumes of 10 mM, 100 mM or 1 M KCl solutions to an initial volume of de-ionized water, and concentrations calculated empirically. Sensor potentials were measured over 15 minute periods at each chloride concentration and average values calculated from data collected over the final minute of exposure to that level, when responses were considered to have fully stabilized. Fig. 3 shows the average response of chloride sensors produced by amperostatic coulometry as a function of electrode charge density. All variants exhibit nearly identical logarithmic responses to chloride concentration, with slight departures from the ideal noticeable at very low chloride concentrations. Fig. 4 shows similar responses for those sensors produced in different chloride solutions. This suggests that the source of chloride is not important, though a slightly lower sensitivity was observed with the sensors produced in HCl. Chloride sensitivity values and electrode offset potentials were calculated from the data and these parameters are summarized in Table 1.

The average responses of chloride sensors produced by the two aSWV techniques are shown in figures 5 and 6. All of these sensors also exhibit nearly perfect logarithmic relationships between electrode potential and chloride ion concentration. Of the two techniques, those sensors produced with asymmetry in potential limit (Fig. 5) demonstrate the more perfect relationship, with no obvious differences associated with the stripping potential used. Of note, there is a slight departure from the ideal logarithmic relationship at low chloride concentrations for sensors produced with

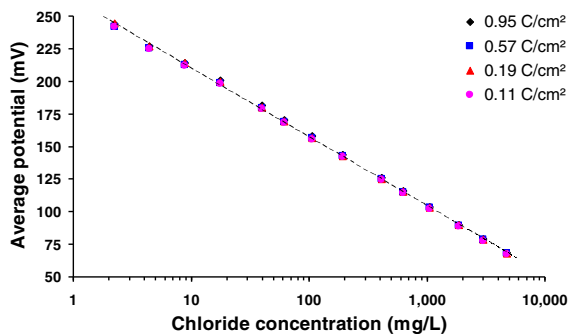


Fig. 3: Average responses for sensors produced by amperostatic coulometry as a function of charge density. Broken line shows trend.

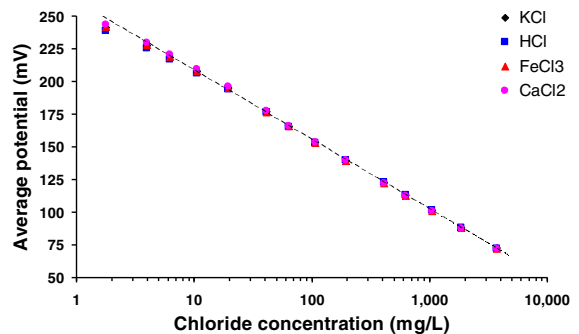


Fig. 4: Average responses for sensors produced by amperostatic coulometry as a function of ion source. Broken line shows trend.

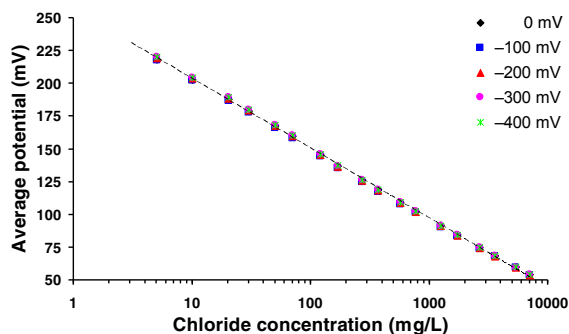


Fig. 5: Average responses for electrodes produced by aSWV as a function of stripping potential. Broken line shows trend.

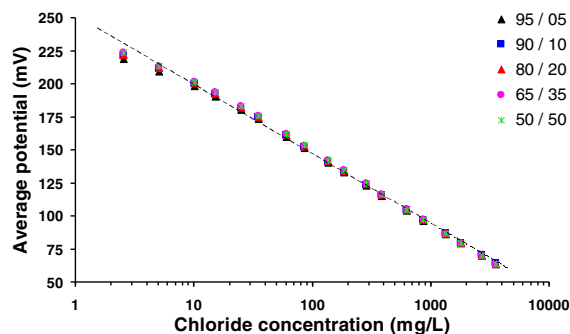


Fig. 6: Average responses for electrodes produced by aSWV as a function of growth/stripping time ratio. Broken line shows trend.

asymmetry in the growth/stripping ratio (Fig. 6), and closer inspection of the data reveals that the degree of this deviation increases with the ratio of growth/stripping time. Table 2 summarizes the chloride sensitivity values and electrode offset potentials calculated from the data for these sensors.

Table 1. Average (n = 4) response parameters for chloride sensors produced by amperostatic coulometry.

Chloride source	Charge density (C/cm <sup>2</sup> )	Sensitivity (mV/pCl)	Offset (mV)	Chloride source	Charge density (C/cm <sup>2</sup> )	Sensitivity (mV/pCl)	Offset (mV)
KCl	0.11	-52.6 ± 0.4	22.3 ± 0.6	KCl	3.0	-52.0 ± 0.1	22.6 ± 1.5
KCl	0.19	-53.1 ± 0.1	22.2 ± 0.2	HCl	3.0	-51.3 ± 1.3	23.6 ± 1.9
KCl	0.57	-52.5 ± 0.3	23.2 ± 0.4	CaCl <sub>2</sub>	3.0	-53.0 ± 1.7	20.4 ± 3.3
KCl	0.95	-53.0 ± 1.5	23.1 ± 2.4	FeCl <sub>3</sub>	3.0	-52.4 ± 0.8	21.4 ± 1.7

Table 2. Average (n = 3) response parameters for chloride sensors produced by asymmetric square wave voltammetry.

Grow / strip time ratio	Stripping potential (mV)	Sensitivity (mV/pCl)	Offset (mV)	Grow / strip time ratio	Stripping potential (mV)	Sensitivity (mV/pCl)	Offset (mV)
95 / 05	-400	-51.7 ± 0.2	14.0 ± 0.1	50 / 50	-400	-53.5 ± 0.1	14.6 ± 0.1
90 / 10	-400	-52.2 ± 0.5	13.5 ± 0.4	50 / 50	-300	-53.5 ± 0.2	14.5 ± 0.1
80 / 20	-400	-52.4 ± 0.6	13.4 ± 0.4	50 / 50	-200	-53.4 ± 0.2	14.4 ± 0.1
65 / 35	-400	-53.0 ± 0.3	12.6 ± 0.5	50 / 50	-100	-52.8 ± 0.9	14.6 ± 0.3
50 / 50	-400	-53.1 ± 0.2	12.5 ± 0.1	50 / 50	0	-52.9 ± 0.4	15.5 ± 0.5

#### 4. Discussion

Comparison of the data presented in Tables 1 and 2 reveals that there are no significant differences in the characterizing parameters of the chloride sensors fabricated, implying electrochemical growth of AgCl is a relatively robust process. The lower offset potential observed in all aSWV type sensors compared to all amperostatic sensors may be due to (encouraged) stripping of electroactive impurities during film growth (e.g. oxides and hydroxides), the presence of which would otherwise erroneously contribute to the electrode potential, suggesting that this is a slightly better electrochemical technique for producing reliable chloride sensors.

#### References

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 [2] Cranny A, Harris NR, Nie M, Wharton JA, Wood RJK, Stokes KR, Screen-printed potentiometric Ag/AgCl chloride sensors: lifetime performance and their use in soil salt measurements, *Sensors and Actuators A* 2011;169:288-94.