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Improved free chlorine amperometric sensor chip for drinking water applications

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Abstract

This paper outlines the advantages of using gold cathodes, in comparison to platinum ones, combined with a series of potential steps that keep the electrode active longer times. A working potential of 0.150 V versus Ag/AgCl (3 MKCl) allows the amperometric determination of free chlorine over the pH range most likely to be found in drinking waters. This pH window spans from pH 5 up to pH 8. The importance of pH and how it can influence the amperometric response inside and outside this narrow pH window is discussed.

Keywords: Hypochlorite; Amperometry; Voltammetry; Drinking water; On-chip electrodes

1. Introduction

Chlorine is probably the most widely used disinfecting agent [1]. In water, it is generally used to ensure pathogen control, but at too high levels it also becomes noxious for humans. Its detection and control is therefore of vital importance. The most usual detection methods rely on the spectrophotometric determination of *N*,*N*-diethyl-*p*-phenylendiamine (DPD) [2,3] but electrochemical methods represent an equally trustworthy alternative. Various groups have developed electrochemical chlorine sensors using different electrode geometries and configurations [4–11] and electrode materials [6,12–14]. Although the most common operation modes involve the use of the working electrode as a cathode, recent reports of anodic detection can also be found [12,15,16]. The amperometric sensor described in this article is based on the reduction of hypochlorous acid/hypochlorite at a gold cathode.

In a previous study, the continuous detection of hypochlorite in tap water was demonstrated at an on-chip Pt disc electrode. [17] The average lifetime of a sensor measuring continuously in tap water was roughly a week. This rather limits the use of such an electrochemical sensor in industrial environments where continuous real time data are needed. Under the controlled conditions of our previous tests, electrode passivation was identified as the main cause of sensor failure.

Due to the unselective nature of amperometric measurements, there are several other sources of potential system failure. Amongst these: (a) the presence of additional and/or unexpected electroactive substances, (b) reference electrode potential shifts and (c) uncontrolled changes in hydrodynamic conditions.

In this work, we address problems associated to electrode passivation by the prolonged action of hypochlorite and the interference by other electroactive substances, namely oxygen.

In general, electrode passivation may be brought about by either adsorption and subsequent build up of organic matter present in the sample matrix (*electrode fouling*), or by the oxidation of the electrode during the course of the main electrochemical process.

It was found previously [17] that the direct reduction of hypochlorite/hypochlorous acid resulted in the eventual passivation of platinum electrodes. This problem could be solved through the regular polishing of the electrode using lapping compounds. However, this is neither a satisfactory option for industrial applications nor feasible for thin-film electrodes fabricated using silicon technologies. Therefore, an in situ cleaning protocol based on a series of potential pulses was devised in order to avoid electrode mechanical polishing while extending the useful life time of these sensors.

For the sake of improved selectivity, platinum was replaced by gold as the thin-film working electrode material. Gold showed

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a higher overpotential for oxygen reduction than platinum. This means that oxygen is reduced at more negative potentials at gold than at platinum electrodes. The first advantage of this is that the chances of overlap between the two reductions (of hypochlorite and of oxygen), particularly on acidification of the sample are minimised, which in turn avoids errors in the estimation of the free chlorine concentration. However, the strong pH dependency of both oxygen and chlorine reduction potentials suggests that overlap of these two signals may still be possible under very low pH conditions as described below. pH is one of the most important factors to consider when measuring free chlorine in a real sample. The pH dependency of the hypochlorite system is described by the following two equations [1,18]:

$$\mathrm{HClO} + \mathrm{H}^+ + 2\mathrm{e}^- \rightleftarrows \mathrm{Cl}^- + \mathrm{H_2O} \quad E = 1.49\,\mathrm{V\ versus\ NHE} \tag{1}$$

$$\mathrm{HClO} \rightleftarrows \mathrm{ClO}^- + \mathrm{H}^+ \quad \mathrm{p}K_\mathrm{a} = 7.5 \tag{2}$$

Eq. (1) implies that the formal potential of the system shifts with pH. From an analytical standpoint, this is not generally a problem for potential sweep techniques, such as cyclic voltammetry, because they allow the estimation of background currents. On the other hand, in the case of amperometric measurements, where the potential is fixed at a given value, no background current corrections are usually possible and a thorough control over sample composition and conditions is required if the measured currents are to be of any real value. However, and despite their shortcomings, amperometric sensors are an attractive option for industrial applications because of the advantages they offer compared to sweep techniques. They allow for continuous and real time measurements, their output signals are easier to analyse and the instrumentation needed is easier and cheaper to build.

2. Experimental

Potassium chloride (KCl), potassium hexacyanoferrate(III) (K_3FeCN_6) and di-sodium hydrogen phosphate anhydrous (K_2HPO_4) salts were purchased from Panreac. Tri-sodium phosphate (K_3PO_4) was purchased from Merck's Laborpreparate (Germany). Potassium hydroxide (KOH) was purchased from Fluka. Sodium hypochlorite solution (NaClO) (available chlorine 10–13%) was obtained from Aldrich. Nitric acid solution (HNO_3, 69%) was obtained form Panreac. All chemicals were analytical reagent grade and aqueous solutions were prepared using ultra pure de-ionized water (DI) (18 MΩ cm).

2.1. Electrode preparation

The on-chip working electrodes used in this study were made using standard photolithographic techniques. A 4 in. diameter silicon wafer was oxidised (800 nm of SiO_2). Titanium (20 nm) and platinum or gold (100 nm) layers were subsequently deposited and patterned by lift-off to form the electrodes and contact pads.

The chips were cut individually from the wafer and mounted on test printed circuit boards. Following the soldering of wires to the connectors, a UV-curable polymer was used as encapsulant. The various processes employed are described in [19,20].

2.2. Apparatus

Cyclic voltammetry experiments were carried out with a PalmSens potentiostat (Palm Instruments BV, Holland) interfaced to a PC and using PalmSens software for Windows®. Amperometric measurements were performed using a Solartron 1287 electrochemical station driven by CorrWare 2.8 software for Windows®.

A Crison Ag/AgCl (3M KCl) was used as reference electrode (RE) unless otherwise stated. pH was monitored using a Hanna Instruments pH300 interfaced to a computer using the supplied HI92000 software.

Flow injection analysis (FIA) experiments were performed using an in-house designed and built cell as described elsewhere [17]. Solution flow was achieved by means of a GILSON MINIPULSE3 peristaltic pump and silicon tubing of 0.8 mm of inner diameter. The solution inlet was placed at less than 0.5 mm distance from the working electrode.

The volumetric flow rate used in this work was $175\,\mathrm{mL\,h^{-1}}$ unless otherwise stated. Due to the small size of the cell used, it was not possible to use a commercial reference electrode and, during flow experiments, a chlorinated Ag wire served as pseudo-reference electrode [21], while a Pt wire was used as counter electrode.

Hypochlorite concentrations were always checked using the spectrophotommetric method based on *N*,*N*-diethyl-*p*-phenylenediamine (Standard Methods name: DPD) [2] using a Hanna Instruments HI95701 Free Chlorine ISM. [22]

3. Results and discussion

3.1. Effect of pH on the hypochlorite system

In the present system, pH is perhaps the most important variable to consider. Tap water pH may range from $5 < \mathrm{pH} < 8$. In our previous report [17], a working potential was found where, within this particular pH range, the observed current corresponds to the two electron mass transport limited reduction of hypochlorite/hypochlorous. This limiting current is virtually constant for a given free chlorine concentration. Within this range, small variations in the current may be attributed to a changing "apparent" diffusion coefficient corresponding to the different $\mathrm{HClO/ClO^-}$ ratios in solution, as per Eq. (2). Since the diffusion coefficients of each species is different [23], their ratio will have an effect on the observed current. This can be shown using a simple model based on two main assumptions: (a) the electrode is equally accessible and (b) the diffusion layer thickness is independent from the diffusion coefficients. Thus, mass transport controlled currents respond to the following equation [24]:

$$I = \frac{nFADc}{\delta} \tag{3}$$

where I is the current in Amperes, F the Faraday constant, A the electrode area, D the diffusion coefficient, δ the thickness of the