Multi-parameter system for marine environmental applications

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Abstract. The contamination of sea waters by pollutants is a subject of growing public concern. The existing monitoring process is costing an estimated 350 million Euros/year in the EU. Most of the detection methods are laboratory-based, which require extensive sample preparation prior to analysis and, hence are not suitable for on-site analysis. Here a multi-sensor system is described for eventual deployment in a port. The system can provide an accurate assessment of the water quality through monitoring a variety of different parameters. Copper detection, conductivity measurements and redox potential measurements are described, and the stability of each sensor in artificial seawater is estimated.

1. Introduction

The established methods for the detection of pollutants in waters are based on sampling and analysis of discrete water samples. The analysis is performed in laboratories located remotely away from the sampling sites and frequently the chemical analysis is carried out with expensive apparatus, such as bench-top spectrometers and chromatographs. The issue with these methods is that, although they function well and provide reliable chemical data, they are laboratory-based, personnel-dependent, time-consuming and expensive. However an emerging research trend in the last 1-2 decades has been the growing interest in research and development of chemical sensors and biosensors which can meet the monitoring needs in polluted water at the point of need. Electrochemical techniques are low-cost, sensitive and both instrumentation and sensors can easily be miniaturised [1-3] which facilitates the development of portable analytical systems. Moreover, by using microelectrode arrays in such systems, it is possible to detect low levels of pollutants without special procedures for sample preparation [4].

The described system includes three types of electrochemical sensors. The first type of sensor relates to detection of chemical pollutants. They are based on amperometric / voltammetric measurements and used for the detection of heavy metals, phenols and dissolved oxygen. The remaining sensors are concerned with monitoring of physical parameters of the seawater including conductivity and the oxido-reduction potential. An impedimetric sensor is used for theseawater conductivity measurements and potentiometric sensor is used for potentiometric measurements of the oxido-reduction potential. All of these sensors have a fast response time which is suitable for a rapidly changing water environment. Integration of all these sensors in the complete system provides not only manifold environmental control of seawater quality but allows also application of data fusion approaches for improving performance of the system. The sensors have initially been fabricated on separate chips; however, the final device will incorporate all devices on one silicon chip as shown in fig. 1. It consists of: working electrode arrays (noted as (1) on Fig. 1 (amperometric/voltammetric measurements,), interdigitated electrode ((2), conductivity) and Pt electrode ((3) oxido-reduction potential) and includes counter electrodes – CE to provide current to the working array and a reference electrode RE to define working array potential. Due to conditions of working in seawater all electrodes (excluding RE) made of platinum, the reference electrode made of silver | silver chloride paste.

This paper presents the detection of copper using voltammetric sensor, the conductivity of artificial seawater using impedimetric sensor and the redox potential in seawater using potentiometric sensor.
2. Materials and Methods

1.1. Fabrication

Arrays of platinum disks were fabricated by standard deposition, etching and lithographic techniques used in silicon microfabrication technology [2]. The first step involved growth of a 1µm thermal silicon oxide layer on a silicon wafer. Titanium (Ti) adhesion layer and platinum (Pt) microelectrodes were then patterned on the surface by lift-off process. This was followed by plasma enhanced chemical vapour deposition of a 500 nm silicon nitride layer. A photoresist was then spun on the silicon nitride passivation layer and the recessed microelectrode arrays on the microelectrochemical cell (500nm recess depth) were then obtained using a photolithographic etch process (Pt-EKC solvent). The silicon nitride over the electrodes was then removed via an octafluorocyclobutane Deep Reactive Ion etch. Following fabrication, the wafers were diced and the electrodes packaged on printed circuit boards (PCB) by attaching the individual chips to the PCB with gold wire bonds and finally protecting the wire bonds and chips edges by covering in a polymeric selective encapsulant (Amicon 50300 HT, Emerson and Cuming) cured at 150°C for 2 hours [2]. To allow a robust connection during testing of the sensor die, a 10 way straight header from AVX interconnect was soldered to the PCB via holes. The corresponding reusable socket had leads attached which connected to the potentiostat channels.

3. RESULTS AND DISCUSSIONS

3.1 Copper detection

Copper is both an essential nutrient and a water contaminant. Its occurrence in seawater is due to natural processes as well as man-related activities such as mining and petroleum refining. Furthermore, copper has replaced tributyl tin compounds in the composition of antifouling paint. Underpotential deposition–stripping voltammetry (UPD-SV) is suitable for the detection of heavy metals in environmental samples [5]. The sensor prototype for Cu detection is shown in Figure 3. The suggested analytical procedure for the detection Cu²⁺ consists of four steps. The first step is the preconditioning of the electrode; its role is to prepare the surface before the cleaning step (second step), which ensures that all the metal ions deposited from previous experiments are dissolved. The third step is the preconcentration stage during which the deposition of metal ions from the seawater onto the surface of the electrode is occurring. Finally, the last step is the detection of the metal ions by redissolution of the metal ions into the seawater. The signal recorded during this step allows the quantification of the metal ions.

Figure 2. (A) Pictures of type 1 sensor. (B) detail of the sensor area. CE stands for counter electrode, WE: for working electrode array and RE for reference electrode. (C) detail of the working electrode array made of 64 microdiscs of 10 µm in radius arranged in a honeycomb layout and with a centre to centre separation of 200 µm.
Figure 3 shows the signal recorded during the detection step for increasing concentration of copper. The peak current was extracted from the different voltammograms and calibration curves for copper were plotted. The peak current values increase linearly with the copper concentration.

![Figure 3. Underpotential deposition – stripping voltammetry and calibration curve for copper in artificial seawater](image)

The limit of detection which was calculated from this calibration curve was estimated at 157 nM which is within the range of measured levels for copper in polluted port areas.

3.2. Stability of Voltammetric sensor

The stability of the sensors over time is essential for operation of autonomous and remote sensing systems. Stable and reliable electrodes indeed allow in-situ detection and monitoring of pollutants levels. Repetitive cyclic voltammetry of 1 mM ferricyanide in artificial seawater was investigated by scanning in the potential window from +0.6 to 0.0 V at a scan rate of 10 mVs⁻¹ every hour for 72 hours. The investigated microelectrochemical cell was immersed in the artificial seawater during the whole duration of the experiment. The stability of the cell was evaluated by observing the limiting current measured, the slope of the sigmoidal wave and the variation of the current at given potentials. The limiting current density versus time is shown in Figure 4. It drops from 302.2 nA.cm⁻² at t= 0 hour down to 270.6 nA.cm⁻² at t= 6 hours. The limiting current density response then drifts slowly to reach 278.8 nA at t= 72 hours. The drift can be due to two factors: the impact of the artificial seawater medium or/and to electrode degradation as a result of repetitive use.

![Figure 4. 73 repetitive cyclic voltammograms of 1 mM ferricyanide in artificial seawater Rest time between experiments was 1 hour. Inset: Variation of the limiting current versus time.](image)

3.3. Conductivity Detection

The impedimetric sensor was characterized using conductivity standard solutions and artificial seawater and impedance measurements where real and imaginary impedance values were recorded over a frequency range 1MHz to 0.1Hz. Figure 5 shows a Nyquist plot of the sensor for three standard solutions with KCl concentrations 0.01M, 0.05M and 1M.

![Figure 5. Nyquist plot for impedimetric sensor in different KCl solutions](image)
3.4. Stability of the Impedimetric sensor

Short term stability in artificial seawater was determined through repeated impedance testing. The variation at increasing frequency was determined using the relation

\[
\text{Var} = \frac{Z_t - Z_{\text{avg}}}{Z_{\text{avg}}} \%
\]

(1),

where \(Z_{\text{avg}}\) is the average impedance value. A maximum variation of 5.4% was observed at 0.1Hz.

Table 1 Variation over frequency sweep for impedimetric sensor

| Variation in total impedance at 1MHz (%) | Variation in total impedance at 10KHz (%) | Variation in total impedance at 100Hz (%) | Variation in total impedance at 10Hz (%) | Variation in total impedance at 0.1Hz (%) |
|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| 1.3                                    | 1.58                                   | 3.56                                   | 4.33                                   | 5.41                                   |

3.5. The Redox Potential sensor

The oxidation-reduction potential is another indicator of water quality and can provide additional information regarding the seawater pollution and be used to compensate readings from the main chemical sensors against interference.

3.6. Stability of the redox sensor

The redox sensor was used to measure the oxidation-reduction potential over 72 hours. A drift of 2.9 mV / hour was observed over the time-frame, indicating that efforts should be concentrated on the stability of the reference electrode.

4. CONCLUSIONS

This paper has described the fabrication of microelectrode arrays of microdisk and interdigitated sensors using UV photolithographic and e-beam lithographic techniques. The microdisk arrays have been characterised for copper detection with a LOD of 157nM. The stability of the arrays has been investigated through a 72 hour repetitive cyclic voltammograms of 1 mM ferricyanide in artificial seawater. A 23nA.cm\(^{-2}\) drift was recorded which could have been due to either the impact from the seawater or electrode degradation with repeated use. The stability of the conductivity sensors was determined through repeated impedance testing in artificial seawater. Dependent on the frequency conditions, a variation of 5.41% at 0.1Hz and 0.5% at 1MHz was determined. The stability of the redox sensors was measured over 72 hours and a drift of 2.9mV/hr was observed. Future efforts will focus on improving the stability of the reference electrode.

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