A novel chemical sensor with multiple all-solid-state electrodes and its application in freshwater environmental monitoring

Zhou, Yifan; Mur, Luis; Edwards, Arwyn; Davies, John; Han, Jiwan; Qin, Huawei; Ye, Ying

Published in:
Water Science and Technology
DOI: 10.2166/wst.2018.310
Publication date: 2018

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the Aberystwyth Research Portal (the Institutional Repository) are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the Aberystwyth Research Portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the Aberystwyth Research Portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

tel: +44 1970 62 2400
e-mail: is@aber.ac.uk

Download date: 14. Jun. 2020
A novel chemical sensor with multiple all-solid-state electrodes and its application in freshwater environmental monitoring

A chemical sensor with multiple electrodes and its application


1 Ocean College, Zhejiang University, Zhoushan, Zhejiang, China, 316021

2 Aberystwyth University, Institute of Biological, Environmental and Rural Sciences, Aberystwyth, Wales, SY23 3DA, UK.

3 Hangzhou Dianzi University: Xiasha Higher Education Zone, Hangzhou, Zhejiang, China, 310018

* communicating author
Abstract

Freshwater quality detection is important for pollution control. Three important components of water quality are pH, ammonia and dissolved H₂S and there is an urgent need of a high-precision sensor for simultaneous and continuous measurement. In this study, all-solid-state electrodes of Eh, pH, NH₄⁺ and S²⁻ were manufactured and mounted to a wireless chemical sensor with multiple parameters. Calibration indicated that pH electrode had a Nernst response with slope of 53.174mV; NH₄⁺ electrode had a detection limit of 10⁻⁵mol/L (Nernst response slope of 53.56mV between 10⁻¹to 10⁻⁴mol/L). Ag/Ag₂S has a detection limit of 10⁻⁷mol/L (Nernst response slope of 28.439mV). The sensor was cylindrical and small with low power consumption and low storage demand to achieve continuous in-situ monitoring for long periods. The sensor was tested for 10 days in streams at Trawsgoed Dairy farm in Aberystwyth, UK. At the intensively farmed Trawsgoed, the concentration of NH₄⁺ in the stream rose sharply after the application of slurry to adjacent fields. Further, the stream was overhung with extensive vegetation and exhibited changes in pH, which correlated with photosynthetic activity. Measurements of S²⁻were stable throughout the week. Our data demonstrates the applicability of our multiple electrode sensor.

Key Word

Multiple electrode sensor; water environment; in-situ monitoring; Ammonium
Introduction

Globally, agriculture is the largest user of fresh water but is also a source of contamination through chemical runoff. Within freshwater, pH, ammonia and dissolved H$_2$S are three important indicators of quality. pH is an important measurement of water chemistry and reflects both characteristics of the underlying bedrock and the amount of plant growth and organic material. The latter reflects the release of CO$_2$ as a result of the decomposition of organic matter and also active respiration, both of which leads to the formation of carbonic acid (H$_2$CO$_3$). Plant and algal growth also reflects run-off of nitrogen (N)-fertilizers, whether synthetic or as biological wastes; leading to the eutrophication of water courses (Ip et al., 2004). These N inputs are reduced to free ammonia(Xu et al., 2008). Dissolved H$_2$S can originate from various sources (coal-based power plants, natural-gas processing, refineries, smelter operation) and can be regarded as a major air pollutant entering the atmosphere and causing acid rain (Primavera et al., 1998). Continuous measurements of dissolved H$_2$S in water is in need to monitor any accidental releases, particularly from industrial sources (Miloshova et al., 2003). Therefore, monitoring pH, dissolved H$_2$S and ammonia; ideally continuously, is very important for the agricultural water environment, drinking water and fresh water. In situ is a particularly attractive target as some ions in water solution are unstable and easily change to other forms.

The traditional methods for ion measurement include ion chromatography (Rey et al., 1998), fluorometry, spectrophotometry (Goyal et al., 1988) and titration(He, 2000). However these methods are time-consuming and cannot be use for continuous in-situ monitoring. Ion selective Electrodes (ISEs), that give a potentiometric signal that obeys the Nernst equation, are currently attracting considerable attention (Mikhelson, 2013). ISEs have a high selectivity to certain ion, and are able to detect low concentrations. Further, ISEs are applicable for in-
1 *situ* monitoring due to their quick response time (Michalska, 2012). The most widely used ISEs are glass electrodes (Gonçalves et al., 2011; Mikhelson, 2013), which contain an internal reference solution. However, these are difficult to miniaturize and are easy to be damage (Chen et al., 2007; Cheng et al., 2011). The development of all-solid-state electrodes represents a considerable recent improvement (Cattrall & Freiser, 1971; Mikhelson, 2013). They have a lower resistivity and smaller than glass electrodes and have eliminated the need for an internal reference solution. The high performance of all-solid-state electrodes makes it possible to integrate these other electrodes for long-term continuous *in-situ* monitoring in water environment.

In this study, we describe the construction of all-solid-state electrodes for Eh, pH, \(\text{NH}_4^+\) and \(\text{S}^2-\), mounted to a wireless chemical sensor with multiple parameters. We demonstrate the sensors efficacy in the continuous *in-situ* measuring of Eh, pH, \(\text{NH}_4^+\) and \(\text{S}^2-\) in freshwater streams in agricultural active farm (Trawsgoed, UK; 52°20’ 38” N, 3°57’ 4” W). Thus, extensive use of this sensor could allow the monitoring of agricultural runoff in varying environments.

**Methods**

**Electrode construction and sensor design**

\(\text{Ir}/\text{Ir(OH)}_x\)-pH electrode preparation and lab test

The Ir wires were ultrasonically cleaned in a HCl bath and then rinsed in deionized water. In three-electrode system of the CHI760D electrochemical workstation, the Ir electrode was used as the working electrode, the Ag/AgCl electrode as the reference electrode and the Pt electrode as the auxiliary electrode. Cyclic voltammetry (CV), with scanning in 5% LiOH solution (0.1 M), was used to form Ir electrode with a layer of Ir(OH)_x film (Zhang et al., 2017).
pH buffer solutions of 4.00, 6.86, 9.18 were used to calibrate the Ir/Ir(OH),-pH electrode. The pH electrode was calibrated using a CHI760D electrochemical workstation.

NH₄⁺ electrode preparation and lab test

A Ag wire was polished with alumina powder and ultrasonically cleaned in a HCl bath. This was rinsed in deionized water and dried in open air. A nano-Ag layer was electroplated to Ag wire for better conductivity. The anode and the cathode of the electroplating system were all Ag wires. A solution of 0.1M AgNO₃ was used as the electrolyte.

The conductive polyaniline (PANI) layer was formed by the three-electrode system. Cyclic voltammetry (CV) method was used in 0.1M aniline hydrochloride. Then the wire was dipped in saturated solution of copolymer aniline(CPANI) and 2,5-dimethoxyanilineas the second layer. Finally, Ammonium ionophore I (6.9%), Potassium tetrakis (4-chlorophenyl) borate (0.7%) and 2-Nitro phenyloctyl ether (92.4%) was dissolved in N,N-Dimethyl formamide (DMF) and the wire dipped into this solution to form the third layer(Huang et al., 2015).

A series of NH₄Cl solution from 1×10⁻¹ to 1×10⁻¹ M were prepared. The NH₄Cl solution consisted of 0.5349 g NH₄Cl and made up to 100 mL in volumetric flask with deionized water to obtain a 1×10⁻¹ M NH₄Cl solution. 1×10⁻¹ M to 1×10⁻¹ M NH₄Cl solution were stepwise diluted by the 1×10⁻¹ M standard NH₄Cl solution with deionized water. The NH₄⁺ electrode was calibrated using a CHI760D electrochemical workstation.

Ag/Ag₂S electrode preparation and laboratory testing
A 3 cm Ag wire was polished and electroplated with a nano-Ag layer using the same method as described in 2.2 and then immersed to the 0.1M Na₂S solution for 10 min. Ag₂S formed the outmost layer of the electrode (Ding et al., 2015).

A series of Na₂S solutions ranging from $1 \times 10^{-7}$ to $1 \times 10^{-1}$ M were prepared. To avoid $S^-$ oxidation, a sulfur antioxidant buffer (SAOB) was prepared in place of deionized water when preparing the Na₂S solution. Stocks of 1L of SAOB contained 80 g of NaOH, 35 g of ascorbic acid (VC), 67 g of EDTA-2Na, and 35 g of NaCl. The Na₂S solution consisted of 0.7804g Na₂S and made up to 100 mL in volumetric flask with SAOB to obtain a $1 \times 10^{-1}$ M Na₂S solution. $1 \times 10^{-1}$ M to $1 \times 10^{-7}$ M Na₂S solutions were stepwise diluted by the $1 \times 10^{-1}$ M standard Na₂S solution with SAOB. The Ag/Ag₂S electrode was calibrated using a CHI760D electrochemical workstation.

Multiple-parameter sensor design

Figure 1 Structural Diagram of Chemical Sensor
Figure 1 shows the structural diagram of chemical sensor. The outer shape is a cylinder with a length of 230mm and 75mm in diameter. The outer covering is made up of 30CrMnSi, which is a compound metal which confers added strength to protect the sensor against environmental impacts. The sensor contains a communication port, a detector part outside and a circuit board and a battery. The pH electrode, NH\textsubscript{4} electrode, Ag/Ag\textsubscript{2}S electrode, Eh electrode and Ag/AgCl reference electrode were integrated into the detector part (Figure 2 (a)). The Eh electrode was made of a platinum wire and Ag/AgCl reference electrode was prepared by melting method (Zhong & Yexiang, 1998). To better connect the electrode to the detector part, the platinum wire and Ir wire were connected to Ag wire by gas welding. The exposed metal parts, which connect electrode and electric wire, were wrapped individually by shrinkable tube and an epoxy resin layer to avoid corrosion and short circuiting.

When the sensor is in use and submerged in water, a semi-hollow cap covers the detector part. The semi-open design of the detector part not only guarantees full contact between electrodes and water but also prevent the chemical membrane being damaged by rapid rushing water and greatly avoid biofouling.
Figure 3 illustrates the working principle of the data acquisition system. First, the chemical sensors detect the chemical signals and convert chemical signals into electrical signals, which then go through the filter, are amplified into the main processor, and stored in a Flash memory function. The watertight connector may be linked to the host computer for real-time communication. The whole data collection can be controlled by the host computer’s software. The built-in clock and switch chip of the processor were calibrated by the host computer software, which also initiates the sensor’s work mode to collect signals. The multi-parameter sensor can then be disconnected from the host computer in the start the work mode of the processor and used for in-situ observations. At the end of the observation period, the multi-parameter sensor and the host computer can be reconnected to read the stored data through the watertight connector.

Figure 2 (b) shows the structure of the circuit board. Each electrode was connected to a certain port from ‘CON1’ to ‘CON 4’ with a reference electrode at the center, which was connected to ‘CON 8’. ‘RS232’ is the communication interface, connecting to signal lines. According to the circuit board design, the real-time data can be stored in a Flash chip when carrying out fieldwork and retrieved later after connecting to software.
The frequency of data collecting can be set at a minimum of 1s or greater intervals. Therefore, the sensor can be used in multiple environments without constraints of distance as the sensor works and store data independently without connecting to a host computer. The two system mode, sleep mode and work mode, consume 1.0mA and 3.5mA electric current respectively. The input impedance of the system is $10^3 \, \Omega (25^\circ C)$, which guarantee long-term use with two AA Li batteries. The data is stored in a Flash chip with 128M bit storage capacity as internal storage. If measuring frequency is set as once per 1 minute, the storage can guarantee 2 years monitoring. When the storage is full, new data will cover old data automatically. Due to its lower power consumption and low storage demand, the sensor can achieve continuous in-situ monitoring for at least 6 months. The circuit board and the batteries are sealed in the cylinder made up of 30CrMnSi, no harmful to the surrounding environment.

Life cycle of whole system is about 2 years, needs service to change electrodes and batteries every 6 months.

Polyaniline (PANI) and Silver nano particle, which are bacteriostatic are used for preparation of $\text{NH}_4^+$ and $\text{Ag}_2\text{S}$ electrodes respectively(Tian, 2010; Zongming Xiu, 2012). The 0.25mm diameter Ir wire used for pH electrode is thinner and hard to be adhered. This avoid problem of biofouling in lifetime.

**Field trial locations**

A ten-day fieldwork was conducted between September 17-26 September 2016 at Trawsgoed Farm, Aberystwyth, UK. Trawsgoed Farm is the location of a 350-cow commercial dairy herd. As such the farm produces a large volume of slurry from its livestock. Several ditches stretch across the farm and feeds into the River Ystwyth some 28 km from its mouth. Given this potential for wide-ranging impact on local water quality, it is appropriate to engage in monitoring streams around this farm.
The multiple-parameter sensor, which can detect Eh, pH, NH₄⁺ and S²⁻, was positioned in the ditch of the farm (52°20′38″ N, 3°57′4″ W). The position has been indicated as red spot in Figure 4. The ditch was about 0.5m deep and 1.0m surrounded with green planets. During the field trial, slurry was applied by shallow injection into the farmland adjacent to this stream on the Sept 18th and Sept 19th. As an independent measure of pH, this was measured at a position close to sensor using a Thermo Scientific Orion, ROSS pH Electrode. pH was measured in around midday on Sep. 19th, 20th, 21st, 22nd, 23rd, 24th, 25th, 26th.

To understand the daily variation of chemical parameters, the sensor was set to collect data every 1 minute during the field trial. The sensor was taken back and connected to host computer to extract the stored data at the end of the each period.
of fieldwork. The obtained potential value was converted to concentration value based on the calibration result. To reduce the effect of any abnormal data, the average of every half an hour was calculated based on the obtain 1 minute measurements.

To allow for the effect of temperature, *in situ* pH data was converted to 25°C pH using the following formula:

\[
pH_{25} = pH_{in\,situ} - 0.0151 \times (25 - T)
\]

where T is temperature from Aberystwyth weather website("Past Weather in Aberystwyth, Wales, United Kingdom," 2016).

**Results and Discussion**

**Electrode Calibration**
Figure 5 Potential-pH response of (a) Ir/Ir(OH)$_x$-pH electrode (b) NH$_4^+$ electrode (c) Ag/Ag$_2$S electrode

Figure 5 (a) shows the potential-pH response of the Ir/Ir(OH)$_x$-pH electrode. The
The slope of the fitting line is 53.174, close to the Nernst theoretical value. The correlation coefficient at $R^2 > 0.996$, indicated good linearity when fitting the calibration curve. Figure 5 (b) shows the calibration results of NH$_4^+$ electrode in NH$_4$Cl solution from 10$^{-5}$ to 10$^{-3}$M. The potential gradient from 10$^{-5}$ to 10$^{-4}$ was a little smaller compared with others, the slope of the fitting line from 10$^{-4}$ to 10$^{-3}$M was 53.56 with a coefficient $R^2 > 0.998$, which is also close to the Nernst theoretical value. The Ag/Ag$_2$S electrode has high detection limit. Figure 5 (c) shows the calibration results in Na$_2$S solution from 10$^{-7}$ to 10$^{-1}$ M. The fitting line was 28.439 with a coefficient $R^2 > 0.997$.

Figure 6 Concentration change between 2016/9/17 and 2016/9/26 in Trawsgoed (a) pH-time (b) Eh(mV)-time (c) log C (NH$_4^+$)(mol/L)-time (d) log C (S$^2$-)(mol/L)-time. The green allow indicates when slurry was applied to adjacent fields and the blue arrow a period of heavy rain.

Measuring environmental pH value change
As an initial indication of sensor performance, the pH detected by the sensor at Trawsgoed farm was compared to that detected by a glass pH electrode with an internal reference solution. The pH values for the measuring period ranged between 6.5 and 7.4 (Figure 6 (a)). Table 1 compared the result of pH value tested by pH probe and sensor the latter showed as red spots in Figure 4. The average difference of pH value between pH probe and Sensor was 0.18, which reveals the accuracy of the pH electrode of the sensor. In table 1, pH given by the probe is in the range between 6.6 to 7.36; while that given by the sensor is between 6.89 to 7.20. It seems that the latter is more stable.

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature (°C)</th>
<th>pH probe</th>
<th>Sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2016/09/19 17:33</td>
<td>16.0</td>
<td>6.75</td>
<td>7.08</td>
</tr>
<tr>
<td>2016/09/20 14:00</td>
<td>18.0</td>
<td>6.60</td>
<td>6.94</td>
</tr>
<tr>
<td>2016/09/21 13:50</td>
<td>18.0</td>
<td>6.95</td>
<td>6.89</td>
</tr>
<tr>
<td>2016/09/22 13:44</td>
<td>16.0</td>
<td>7.14</td>
<td>6.94</td>
</tr>
<tr>
<td>2016/09/23 14:40</td>
<td>17.6</td>
<td>7.16</td>
<td>7.09</td>
</tr>
<tr>
<td>2016/09/24 10:44</td>
<td>17.7</td>
<td>7.07</td>
<td>7.08</td>
</tr>
<tr>
<td>2016/09/25 10:00</td>
<td>13.0</td>
<td>7.32</td>
<td>7.07</td>
</tr>
<tr>
<td>2016/09/26 11:52</td>
<td>13.9</td>
<td>7.36</td>
<td>7.20</td>
</tr>
</tbody>
</table>

1 pH value given by Thermo Scientific Orion, ROSS pH Electrode
2 pH value given by the sensor
Examine the sensor derived pH values over a diurnal cycle indicated a regular daytime rhythm (Figure 7). It decreased to the lowest value at around pH 6.5 at ~6:40 AM in the morning and increases to a peak at around 7.2 at 14:00 PM in the afternoon. Given that the sensor was located in an area of dense vegetation, this feature almost certainly reflected the shifting balance between respiration and photosynthesis. At night, plants absorb oxygen and produce carbon dioxide because of respiration to increase of \( \text{H}_2\text{CO}_3 \) in water resulting in a decrease of pH. During daylight, plants absorb carbon dioxide and produce oxygen because of photosynthesis leading to a relative decline in \( \text{H}_2\text{CO}_3 \) and increase in pH. The fact that this pattern was easily detected by the sensor is an indicator of its sensitivity in the detection of pH.

**Between pH-Eh.**

Comparing Figure 6(a) and Figure 6(b) shows how pH and Eh show contrasting trends; thus, Eh increases when pH decreases and decreases when pH rises. This
fits the negative correlation functional relationship between Eh and pH (Brookins, 1988): \[ \text{Eh} = A - 0.059 \text{pH}, \] where A is a constant.

**NH}_4^+ concentration change**

The concentration of NH}_4^+ proved at Trawsgoed farm (Figure 6 (c)) proved to be stable at \( \sim 1.0 \times 10^{-5} \text{M} \) for the first two days of the measuring period. However, immediately after the injection of slurry into neighboring fields, the NH}_4^+ concentration rose sharply to \( 1.6 \times 10^{-2} \text{M} \) (Sep. 19\text{th}, 2016). During the following days, this concentration appeared to be being diluted due to the continual flow of water in the area so that the NH}_4^+ concentration fell progressively to \( 3.9 \times 10^{-4} \text{M} \) by Sep. 21\text{st}. There was a rapidly decrease to \( 1.6 \times 10^{-5} \text{M} \) which correlated with a rain shower in Sep. 21\text{st} evening which would have appeared to accelerate the dilution process. These results clearly indicate that the application of slurry increases the concentration of NH}_4^+ in the stream and most likely in the Ystwyth River to which it is a tributary.

**4.5 S}_2^- concentration change**

The concentration of S}_2^- fluctuated slightly but average to \( \sim 1.0 \times 10^{-6} \text{M} \) (Figure 6 (d)). This was quite a low concentration, which the application of slurry did not significantly change in the water.

**Conclusions**

An all-solid-state electrodes of Eh, pH, NH}_4^+ and S}_2^- was manufactured and mounted to a wireless chemical sensor with multiple parameters. Under laboratory conditions we demonstrated continuous and simultaneous measurement of Eh, pH, NH}_4^+ and S}_2^-.
The sensor was field tested in streams at Trawsgoed farm in Aberystwyth, UK. The result in Trawsgoed indicates that pH value exhibits regular daytime fluctuations due to plant metabolism. The average difference of pH value between a commercial pH probe and the constructed sensor was only 0.18. The trends of pH and Eh stay fitted with the known negative correlation functional relationship between Eh and pH. The concentration of NH$_4^+$ rose sharply when slurry was applied to neighboring fields.

From above, the electrodes of sensor show high accuracy and sensitivity to certain ions. Regarding to the feature of small volume, less power consumption and low storage demand, the sensor will have a broad application in water environment detection.

**Acknowledgements**

This work was supported by Open Research Fund of Laboratory of Marine Ecosystem and Biochemistry, SOA (LMEB201701) and UK-China Joint Research and Innovation Partnership Fund (PhD Placement Programme). The authors would like to thank the staff at Trawsgoed Farm sites (Aberystwyth University) for their help during the measuring periods.
References


Ding, Q., Pan, Y.-w., Huang, Y.-f., Chen, C.-T. A., & Ye, Y. 2015 The optimization of Ag/Ag2S electrode using carrier electroplating of nano silver particles and its preliminary application to offshore Kueishan Tao, Taiwan. *Continental Shelf Research,* 111, 262-267. doi:10.1016/j.csr.2015.08.018


Miloshova, M., Baltes, D., & Bychkov, E. 2003 New chalcogenide glass chemical


