Development of a reliable microelectrode dissolved oxygen sensor

Maciej Sosna a, Guy Denuault a,*, Robin W. Pascal b, Ralf D. Prien c, Matt Mowlem b

a School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK
b National Oceanography Centre, Southampton, University of Southampton, Waterfront Campus, European Way, Southampton SO14 3ZH, UK
c Baltic Sea Research Institute, Seestraße 15, 18119 Rostock-Warnemünde, Germany

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Abstract

This article reports the results of a careful experimental and analytical investigation which led to the development of an accurate and reproducible microelectrode dissolved oxygen sensor. Primarily designed for oceanographic applications but also applicable to environmental and water process monitoring, the sensor measures the diffusion controlled current to a bare Pt microdisc electrode for the reduction of oxygen. A successful reconditioning potential waveform is reported which yields a very stable amperometric response over continuous operation, with a maximum deviation of the limiting current under 1.5% over 24 h. An automated calibration method developed to accurately characterise the electrodes is described. Excellent linearity is obtained for all electrodes tested and in each case, the number of apparent electrons for the reduction of oxygen is reported. As an alternative to calibration, an analytical treatment which accounts for temperature and salinity effects is given to calculate the dissolved oxygen concentration directly from the limiting current. While the analytical approach yields a concentration relative error circa 11% for a 50 μm diameter Pt disc, the calibration, has lower errors and yields a detection limit down to 0.9 μM with the same disc. Although this investigation builds on established principles, this article describes, for the first time, the conditions required to obtain accurate and reproducible measurements and provides an estimate of their precision. Preliminary field trials to measure oxygen depth profiles in the ocean have proved very encouraging [R. Prien, R. Pascal, M. Mowlem, G. Denuault, M. Sosna, Development and first results of a new fast response microelectrode DO-sensor, in Oceans 2005—Europe, Vols. 1 and 2, 2005, pp. 744–747].

Keywords: Dissolved oxygen; Amperometric oxygen sensor; Calibration; Microelectrode; Microdisc; In situ measurements

1. Introduction

The concentration of dissolved oxygen (DO) is a vital parameter in industrial, physiological and environmental systems. Continuous in situ monitoring of oxygen levels is needed, often in conditions where maintenance of the sensor is not possible. Particularly in marine applications, a successful sensor has to cope with high salinity and extreme pressures over extended periods of continuous operation, e.g. when recording [O2]-depth profile or in sediments research. Marine in situ sensors, including dissolved oxygen sensors were recently reviewed [2–4]. Amongst those, Clark’s [5] membrane covered amperometric DO sensors are the most common. Also regularly employed are unshielded microelectrodes operated in voltammetric mode with oxygen detected along with other species [6–8]. Trials of bare microdisc DO sensors on moving CTD (conductivity, temperature, depth) probes [9,10] have not been successfully implemented in water column profiling. In contrast, amperometric microelectrode sensors, membrane covered or bare, are routinely used in sediment research [6,7,11–19]. There is a renewed demand for accurate, durable and low maintenance marine DO sensors, not least in studies of climate change. In the marine environment dissolved oxygen concentration varies from near anoxic [20,21] to supersaturated [22]. However typical oxygen profiles will have values in the range 100–300 μM [23]. Required sensor performance is highly dependent on the application. In profiling sub μM resolution is sufficient. Sensors deployed on moorings for long-term studies require precision better than 2 μM, whilst short-term stability and high (<0.1 μM) resolution is required for incubators and sediment probes.

* Corresponding author. Tel.: +44 23 8059 2154.
E-mail address: gd@soton.ac.uk (G. Denuault).

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A reliable method of oxygen calibration is also crucial for the consistency of the measurements. A common approach involves bubbling a gas or combination of gases to control the DO level. This requires either commercial gas mixtures or a calibrated gas mixer. DO sensor manufacturers employ two point calibrations with anoxic and saturated solutions. Unless an independent analysis (Winkler titration) can be performed, the preparation of these standards relies on the precise knowledge of the solubility of oxygen in the test solution. Other approaches generate oxygen in situ, by electrogeneration [24,25] or catalytic decomposition of hydrogen peroxide [26]. These methods however require the exact knowledge of the reactions efficiency and are complicated by the need to introduce additional instrumentation to the system or chemical agents to the solution.

This article reports on the development of a robust, low maintenance, accurate and reproducible amperometric DO sensor. Although the sensor is intended for CTD profilers (and other marine applications including continuous monitoring of DO on moorings and bouys) it can be easily adapted to less harsh conditions where measurements of DO are needed to assess water quality. The difficulties inherent to marine measurements impose severe constraints. In the field the use of membranes (to control the rate of oxygen transport to the electrode) can cause poor sensor performance. Membranes: are easily blocked; are inherently fragile; do not lend themselves to reconditioning; require regular replacement; and exhibit decreasing permeability with pressure. The alternative chosen here is based on bare microdisc electrodes. Their intrinsic characteristics [27–30] make them suitable for in situ sensing: When their radius \( a \) is less than circa 50 \( \mu \)m, edge effects significantly enhance the rate of diffusion and lead to the rapid establishment\(^1\) of a diffusion layer with quasi-hemispherical geometry and to a steady state diffusion limited current. This steady state current is determined by the geometry and dimensions of the electrode hence alleviating the need for a membrane. Steady state diffusion limited currents for oxygen reduction are readily obtained at microdisc electrodes and therefore provide a means to directly determine the dissolved oxygen concentration. Another reason for using microelectrodes in sensing is their small electroactive area which yields very small currents, typically pA to \( \mu \)A, sufficiently small to keep the reference electrode ideally polarised and allow the use of two-electrode arrangements. This simplifies the electronics and results in low power consumption, an essential feature in field applications. Some commercially available DO sensors employ microelectrodes but covered with membranes [31,32]. This is most likely to improve selectivity and eliminate the effect of convection when operating in non-quiescent solutions. Although the diffusion layer thickness is small (circa 10\( a \)), this is sufficiently large, even with micrometer size discs, for the limiting current to be affected by convection. For oceanographic applications we designed a simple stop-flow system to eliminate convection during the measurements [1]. The details of the sensor implemented on a CTD and an analysis of the oxygen profiles recorded to full ocean depth will be reported in a subsequent article.

Here we describe and analyse the significant improvements made to the performance of membrane-free platinum microdisc oxygen sensing cathodes. In particular, we report the operational conditions which lead to a reproducible response and describe an automated calibration system to accurately determine the apparent number of electrons during oxygen reduction. We present an analytical treatment for the direct determination of the dissolved oxygen concentration from the amperometric response. Finally we provide estimates of the measurement accuracy for both calibration and analytical approaches.

2. Experimental

2.1. Solutions, electrodes and instrumentation

All solutions were prepared with purified water obtained from a Whatmann purification system. The water conductivity was less than 0.1 \( \mu \)S cm\(^{-1} \). \( \text{NaCl} \) (Analar, BDH), \( \text{KCl} \) (Aristar, BDH), \( \text{KI} \) (M&B), starch (M&B), \( \text{KIO}_3 \) (Avocado), \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) (Lancaster), \( \text{NaOH} \) (BDH), \( \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \) (Timstar Laboratory Supplies Ltd.), \( \text{Na}_2\text{SO}_3 \cdot 5\text{H}_2\text{O} \) (Timstar Laboratory Supplies Ltd.) and \( \text{Ru(NH}_3)_6\text{Cl}_3 \) (Aldrich) were used as received, without further purification. Sulphuric acid solutions were made with Aristar grade \( \text{H}_2\text{SO}_4 \) (BDH). Argon and oxygen were from BOC Gases.

All experiments were conducted in a two-electrode system with a \( \text{Hg/Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4 \) (sat.) electrode (SMSE) as the reference electrode. All potentials are quoted with respect to it. Working microdisc electrodes were prepared using commonly employed procedures [33]. A platinum microwire (Goodfellow Metals) was sealed in a soda glass pipette and the connection with a thick copper wire was made with indium (Aldrich). For lab work, the electrode was left as is whereas for oceanographic measurements, the microelectrode was further cast in epoxy within a copper tube acting as the counter—reference electrode. This configuration was found to provide adequate electrical shielding to the working microdisc [1]. In all cases wiring to the current follower was kept as short as possible and made with BNC cables. The pipette tip was polished with SiC papers (grades 320, 600 and 1200) to reveal the microdisc and subsequently with alumina slurries (grain size 1.0 and 0.3 \( \mu \)m, Buehler) on a polishing cloth (Buehler). The electrode radius was determined from a steady state voltammogram for the reduction of 5 \( \text{mM} \) \( \text{Ru(NH}_3)_6\text{Cl}_3 \) in deoxygenated aqueous electrolyte, 250 \( \text{mM} \) \( \text{KCl} \). Before each experiment, the electrodes were polished with 0.3 \( \mu \)m alumina paste and cycled in 1 M \( \text{H}_2\text{SO}_4 \) between oxygen and hydrogen evolution until a stable voltammogram typical of Pt in acid was obtained.

The measurements were performed using a waveform generator (Model PPR1, Hi-Tek Instruments, UK) and a home built current follower. The data were acquired with a PC running LabView\textsuperscript{®} software and processed using a commercially available calculation package.

\(^{1}\) For a microdisc, the characteristic diffusion time is given by \( a^2/D \) where \( a \) is the radius of the disc and \( D \) is the diffusion coefficient of the reacting species. With a 12.5 \( \mu \)m radius electrode and a diffusion coefficient of \( 10^{-6} \text{ cm}^2 \text{ s}^{-1} \), typical for diffusion in aqueous solution, the diffusion time is of the order of 1.5 s.
2.2. Microelectrode DO sensor calibration

A schematic of the calibration system is shown in Fig. 1. It consists of three vessels, all filled with the same test solution: a humidifier (A), an oxygen saturated solution reservoir (B) and a measurement cell (C). The ensemble is made of glass, including the tubing connecting the vessels, which is critical and enables transport of solutions without loss or gain of oxygen. The solutions are maintained at a constant temperature using a thermostatic bath (Grant, W14). The measurement cell containing the working and reference electrodes is completely filled (it is imperative to remove all bubbles) with the test solution and sealed to prevent any contact with a gaseous phase. It is also equipped with a glass coated stirring bar. Teflon stirring bars were not used due to the reported oxygen uptake/release by Teflon. The inlet and outlet of the measurement cell are a thin capillary (D) and a thin channel glass connector (E), respectively. Both have a diameter of approximately 0.5 mm which prevents mixing of the contained solution with the solution in the measuring cell. Finally, downstream of the measuring cell a software controlled solenoid pump (Model 120SPI, Bio-Chem Valve Inc., USA) is fitted. This removes a fixed volume from the measurement cell and this volume is replaced by the same volume of oxygen saturated solution. After each addition the solution is homogenised by stirring for 2 min. After 2 min of rest a series of current readings are taken with the microelectrode. The effectiveness of stirring was confirmed by adding a small amount of ink into the cell. The argon feed neck (F) can also be used to introduce another capillary inlet connected to a vessel containing oxygen free solution, which allows performance of a ‘backwards’ calibration, i.e. from high to low oxygen concentration.

The calibration of the sensor is then performed by automatically adding volumes of solution B to solution C, which initially contains no oxygen. Each time the pump is activated, it removes a certain volume from the cell and this volume is replaced by the same volume of oxygen saturated solution. After each addition the solution is homogenised by stirring for 2 min. After 2 min of rest a series of current readings are taken with the microelectrode. The effectiveness of stirring was confirmed by adding a small amount of ink into the cell. The argon feed neck (F) can also be used to introduce another capillary inlet connected to a vessel containing oxygen free solution, which allows performance of a ‘backwards’ calibration, i.e. from high to low oxygen concentration.

The concentration of oxygen in the cell depends on the number of additions ($i$), on the concentration of oxygen in the oxygen saturated solution ($c_{\text{sat}}$), on the volume exchanged (injected/removed) ($V_{\text{ex}}$) and on the total volume of the measuring cell ($V_{\text{tot}}$). The latter is determined prior to the experiment by weighing the fully assembled measurement cell both empty and filled with a solution of known density. After the $i$th addition, the oxygen concentration in the cell is given by

$$c_i = c_{i-1} + \frac{c_{\text{sat}}}{V_{\text{tot}}} - \frac{c_{i-1}V_{\text{ex}}}{V_{\text{tot}}}$$

or generally

$$c_i = c_{\text{sat}} \frac{V_{\text{ex}}}{V_{\text{tot}}} \sum_{k=0}^{i-1} \left(1 - \frac{V_{\text{ex}}}{V_{\text{tot}}} \right)^k$$

where $k$ is the number of additions made. Eqs. (1) or (2) are used to construct calibration plots, see data analysis section. Unlike traditional calibration procedures which typically rely on two or three points (anoxic and air or oxygen saturated solutions) the present procedure allows a very large number of points due to the small stroke volume of the pump piston and its control using

![Fig. 1. Schematic representation of the calibration system. A: humidifier, B: saturated solution reservoir, C: measurement cell, D: inlet capillary, E: outlet connector, F: argon feed neck, G: valve, H: oxygen feed, WE: working electrode, and RE: reference electrode.](image)
software. The number of piston cycles determines the concentration increment while the number of pump action determines the range. It has to be stressed however, that in order to rely on the above equations the exchanged volume \( V_{\text{ex}} \) has to be sufficiently small, so that none of the oxygen added from the saturated solution is removed from the system during one pumping action. Also great care must be taken not to trap any bubbles in the measuring cell and the connecting tubing, while filling or purging the cell with argon. Any trapped bubble would impair the solution volume and cause some of the oxygen to diffuse from the solution into the inert gas bubble.

This calibration has the merit of requiring bubbling only at the start. Once the reservoir has been saturated with oxygen the automated approach makes it possible to rapidly perform a multiple point calibration with programmable DO increments. We are not aware of such approach having previously been reported.

### 3.2. Microelectrode DO sensor

**DO in situ** measurements typically require the electrode to operate for hours or days without maintenance. But platinum electrodes are known to lose their activity towards oxygen reduction when operated continuously over extended periods of time [38,39]. In addition interference can arise from heavy metal traces [39] which poison the platinum cathode by electroplating at the potential where oxygen is reduced. A reconditioning procedure is therefore necessary to maintain a stable response. Since any form of mechanical or chemical conditioning is excluded the electrode is reconditioned electrochemically by applying a suitable potential waveform. Pletcher and Sotiropoulos [39] used repetitive fast potential sweeps and also reported the use of steps to recondition the platinum surface. To keep the electronic circuitry simple we used a potential square wave to recondition the microelectrode. The waveform consists of a long step during which the current for the reduction of dissolved oxygen is recorded and of a short step to recondition the electrode surface. The potential waveform together with a typical current response is shown in Fig. 2.

The potential values were chosen on the basis of voltammetry in the model solution of 0.5 M NaCl with the measuring potential lying in the centre of the oxygen reduction plateau at \(-1.05 \text{ V}\) (Fig. 3) and the ‘cleaning’ potential in the foot of the platinum oxide formation region (not shown).

Several values of the cleaning potential (between 0.1 and 0.5 V) were tested by assessing the long-term stability of the electrode response and the effect of the extended operation on the electrode surface state. The best results were obtained with a waveform consisting of a \(\sim 12 \text{ s}\) measuring step and a 1 s cleaning step at 0.2 V. The duration of the measurement step is a compromise: it is sufficiently long to obtain a steady state response, but limited to avoid the contribution of natural convection. The duration of the cleaning step was arbitrarily chosen and was not further optimised. The limiting current can be taken at the end of the measuring step or as an average of the last few seconds. Either way, this waveform provides one measurement every 13 s. The electrode response (Fig. 4a) shows excellent stability over a trial period of 24 h of continuous operation (standard deviation of the limiting current \(\text{circa} 0.7\%\)). The effect of the prolonged use on the electrode was evaluated by cyclic voltammetry in 1 M H\(_2\)SO\(_4\) before and after the experiment (Fig. 4b). The surface roughness of the electrode, calculated from hydrogen desorption peaks, was observed to increase threefold; this however does not affect the magnitude of the limiting current for oxygen reduction.

The choice of platinum instead of gold as cathode material is driven by the behaviour of the electrode during the cleaning step. Gold is attractive because it promotes the two electron reduction of oxygen [40] however in 500 mM NaCl gold gradually dissolves when stepped to the beginning of gold oxide formation, the microdisc recesses and the amperometric response decreases. In the same conditions, platinum roughens but does not dissolve. If a lower cleaning potential is used the gold electrode response decays over hours of continuous operation. In low chlorinity media, a gold cathode survives the reconditioning step and can be successfully used to monitor dissolved oxygen (results not shown). In addition, experiments carried out with
salt concentrations ranging from 0 to 500 mM showed that the voltammetric wave for oxygen reduction shifted negatively by as much as 300 mV on gold compared to 50 mV on platinum.

3.3. Data analysis

As an alternative to calibration, the concentration of dissolved oxygen can be directly calculated from the microelectrode response and from the equation for the diffusion controlled limiting current \(i_{\text{lim}}\) at a microdisc:

\[
i_{\text{lim}} = 4n_{\text{app}}FD_{O_2}ac\tag{3}
\]

where \(n_{\text{app}}\) is the apparent number of electrons transferred during oxygen reduction reaction, \(F\) the Faraday constant, \(D_{O_2}\) the dissolved oxygen diffusion coefficient, \(a\) the microdisc radius and \(c\) is the dissolved oxygen concentration. While the electrode radius is constant and can be predetermined, both \(n_{\text{app}}\) and \(D_{O_2}\) depend on other parameters.

To calculate \(D_{O_2}\), accurately, its dependence on the electrolyte composition and temperature is needed. An appropriate equation was derived by Akita [41] on the basis of experimental data for 18 species of cations and 13 species of anions. For the simple case of a single 1:1 salt solution it has the following form:

\[
D_{O_2} = \left(\frac{K}{h}\right) \left(\frac{V}{N_0}\right)^{2/3} T \exp\left(-\frac{\Delta \alpha x_+ + \Delta \beta x_- + \gamma}{RT}\right)\tag{4}
\]

where

\[
V = (C_+ + C_- + C_{H_2O})^{-1}\tag{5}
\]

and

\[
C_{H_2O} = \frac{\rho - M_+C_+ - M_-C_-}{0.01802}\tag{6}
\]

where \(\kappa\) is the Boltzmann’s constant, \(h\) the Planck’s constant, \(V\) the molar volume of the solution, \(N_0\) the Avogadro’s number, \(x_i\) the mole fraction of species \(i\), \(C_i\) the molar concentration of species \(i\), \(\rho\) the density of the solution, and \(M_i\) is the formula weight of species \(i\). \(\alpha, \beta, \gamma\) are temperature independent components of the free energy of activation of diffusing solute in aqueous solution, respectively due to cation (\(\alpha\)), anion (\(\beta\)) and water (\(\gamma\)). \(\Delta \alpha, \Delta \beta\) are values defined by \(\alpha \sim \gamma\) and \(\beta \sim \gamma\), respectively. Whereas \(\alpha\) and \(\beta\) are tabulated, \(\gamma\) can be determined from the measurement of the diffusion coefficient of oxygen in pure water \(D_w\) when (4) simplifies to (7):

\[
D_w = \left(\frac{K}{h}\right) \left(\frac{V_w}{N_0}\right)^{2/3} T \exp\left(-\frac{\gamma}{RT}\right)\tag{7}
\]

where \(V_w\) is the value of \(V\) for pure water. The literature values of \(D_{O_2}\) in pure water average to \(\sim 2.20 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\) at 25°C. In this work all the data were processed using \(D_w = 2.11 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\) at 22°C, from Ho et al. [42], and yielded \(\gamma = 13,835 \text{ J mol}^{-1}\). Eqs. (6)–(9) predict the value of \(D_{O_2}\), provided the oxygen diffusion coefficient in pure water and the solution density are known. While in the laboratory all the parameters needed to calculate \(D_{O_2}\) are known, or can be determined, the processing of field data requires independent measurements. In oceanographic applications this is performed by a collocated CTD probe. In this case, the density is calculated from salinity \((S)\), temperature \((T)\) and pressure \((p)\) readings using the equation of state for seawater [43]. The salinity also gives information on the total quantity of ionic matter dissolved. This is in turn modelled as an equivalent sodium chloride solution to calculate the diffusion coefficient. Taking into account the fact that the main component of seawater is NaCl, and the variation of salinity is very small regardless of location, the errors resulting from such approximation are negligible in comparison with uncertainties on e.g. electrode radius or \(D_w\).

The other variable to consider is \(n_{\text{app}}\) as it strongly depends on the mass transport conditions. It is well recognised that oxygen reduction is not a straight forward reaction. It can proceed via parallel pathways [44] that include intermediates and the final products depend on the reaction conditions and electrode material. When microelectrodes are used, \(n_{\text{app}}\) can vary between 2 (reduction to hydrogen peroxide) and 4 (reduction to water). Smaller electrode radii yield higher mass transfer coefficients \(k_{\text{in}} \approx D/a\) due to a higher contribution of radial diffusion to the transport of the reactant to and from the electrode. In cases of high \(k_{\text{in}}\), a fraction of intermediate, \(H_2O_2\), diffuses away from
the microdisc before it can be further reduced to water. The variation of $n_{\text{app}}$ with $k_m$ was reported [45] on the basis of both microelectrode and rotating disc electrode studies. In the present investigation $n_{\text{app}}$ was determined from calibrations, with $D_{O_2}$ calculated as described above.

A family of calibration curves in 0.5 M NaCl at 25 °C using a range of microdisc radii is shown in Fig. 5. The previously described potential waveform was applied to the electrode continuously throughout the duration of the calibration procedure. The sensor shows excellent linearity with correlation factors $R > 0.999$ regardless of the electrode radius. Each experiment also involved a measurement in the oxygen saturated solution. The recorded limiting currents were within few percents of the trend-line extrapolated from the calibration points (Fig. 5, inset). This clearly indicates an excellent linearity over the full range from no oxygen to full saturation.

In each case $n_{\text{app}}$ was calculated from the slope of the curve:

$$\text{slope} = 4n_{\text{app}} F D_{O_2} a$$  \hspace{1cm} (8)

The values obtained show a good agreement with earlier results, see Table 1.

Although the intercepts shown in Fig. 5 are very close to zero, the sensor response shows a residual current in absence of oxygen. This can be due to several reasons: (1) remains of oxygen due to imperfection (or limits) of deoxygenation procedure (argon purging), (2) impurities from the salt used (the residual currents correspond to 3.2, 2.7 and 1.2% of air saturation in Analar NaCl, Aristar NaCl and pure water, respectively), (3) a voltage offset of the electronic amplifier (measured as 1 mV).

Table 2 summarises the key quantities obtained from calibrations of various radii microelectrodes at 25 °C, which allow calculation of the oxygen concentration directly from the microelectrode current.

For the two largest electrodes these errors are below 4% down to 50 μM. This is remarkable for microelectrode experiments and indicates the effectiveness of the preconditioning procedure. The somewhat larger error (below 6%) observed with the smallest electrode is due to the difficulty in determining the electrode radius accurately.

While the values given above can serve to determine the dissolved oxygen concentration in seawater and media of similar salinity, there is a need for calibration when the measurement is performed under significantly different conditions (e.g. fresh

Table 1

<table>
<thead>
<tr>
<th>Radius (μm)</th>
<th>$n_{\text{app}}$</th>
<th>Radius (μm)</th>
<th>$n_{\text{app}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.68 ± 0.17</td>
<td>2.64 ± 0.12</td>
<td>25</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>12.08 ± 0.37</td>
<td>3.26 ± 0.13</td>
<td>12.5</td>
<td>3.3 ± 0.1</td>
</tr>
<tr>
<td>24.54 ± 0.71</td>
<td>3.62 ± 0.09</td>
<td>20</td>
<td>3.7 ± 0.1</td>
</tr>
</tbody>
</table>

The quoted errors are based on the standard error of the calibration curves and the error from the electrode radius determination. Due to a lack of data on error estimates on $D_{O_2}$, the $D_{O_2}$ uncertainty is not taken into account.

Table 2

<table>
<thead>
<tr>
<th>Radius (μm)</th>
<th>Slope (sensitivity) (pA μM$^{-1}$)</th>
<th>Intercept (pA)</th>
<th>Detection limit (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.68 ± 0.17</td>
<td>10.3 ± 0.1</td>
<td>29 ± 14</td>
<td>8.1</td>
</tr>
<tr>
<td>12.08 ± 0.37</td>
<td>32.8 ± 0.2</td>
<td>540 ± 3</td>
<td>2.9</td>
</tr>
<tr>
<td>24.54 ± 0.71</td>
<td>74.0 ± 0.1</td>
<td>640 ± 1</td>
<td>0.9</td>
</tr>
</tbody>
</table>
water). On the basis of known salinity and temperature, \( D_{O_2} \) can be determined and the product \( a \times n_{app} \) can be obtained from the measured slope, giving all the necessary parameters to calculate the oxygen concentration from the limiting current.

The analytical equation for determination of a DO concentration (accounting for temperature, water density, salinity, \( D_{O_2} \) in pure water, the apparent number of electrons, the measured electroactive radii, and the limiting electrode current) is given by substituting (4) and (7) in (3):

\[
c = \frac{i_{lim} \exp((\Delta \alpha x_+ + \Delta \beta x_-)/RT)}{4n_{app} F a D_w (V/V_w)^{2/5}}
\]

(9)

The relative error in concentration using this approach (by total differential error analysis of (9), division by (9) and neglecting insignificant errors on \( V, V_w, \alpha, \beta, x_+, \) and \( x_- \)) is

\[
\frac{\Delta c}{c} = \frac{\Delta i_{lim}}{i_{lim}} + \frac{\Delta n_{app}}{n_{app}} + \frac{\Delta a}{a} + \frac{\Delta D_w}{D_w} + \frac{\Delta T}{T^2}
\]

(10)

The calculated errors for the different electrode radii are 15\%, 14\%, and 11\% for \( a = 5, 12.5, \) and 25 \( \mu m \), respectively and are dominated by uncertainty in the electroactive radii, and the oxygen diffusion coefficient in pure water.

3.4. Field trials

To test performance in the field, a dissolved oxygen sensor based on an unshielded Pt microdisc was constructed and used on a CTD profiler during RRS Discovery cruise D279 [1]. To remove the effect of convection, the microdisc electrode was inserted in a simple cell into which fresh solution was pumped during the reconditioning step. The pump was located downstream of the cell and acted as a valve to stop the flow of solution during the reconditioning step. Several deployments yielded good quality \([O_2]\)-depth profiles. An analysis of the \([O_2]\)-depth profiles recorded and a detailed description of the stopped—flow cell and sensor electronics, will be presented in a forthcoming article.

4. Conclusions

Starting from the established principles of amperometric sensing at microdisc electrodes we have investigated parameters leading to improved performance and developed a dissolved oxygen sensor capable of operating reliably and accurately under real working conditions. In particular we have determined cleaning conditions which produce a stable amperometric response over continuous operation. To obtain an accurate relationship between the electrode current and the dissolved oxygen concentration we have developed an automated calibration which provides a fine control of DO increments and range. As an alternative to calibration we propose an analytical approach which accounts for temperature and salinity effects and gives a direct value of the dissolved oxygen concentration from the electrode current. The treatment relies on the number of apparent electrons we have determined through calibration and tabulated for different microdisc radii. The analytical approach requires the knowledge of temperature, water density, salinity, \( D_{O_2} \), in pure water, \( a \), and \( n_{app} \) from Table 1. For different radii, tabulated values can be interpolated. The relative accuracy ranges from 15\% for the smallest to 11\% for the largest microdisc. The determination of the dissolved oxygen concentration is more accurate via calibration but this requires that the calibration be performed in a body of water with similar density and salinity to the test sample.

Acknowledgement

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Biographies

Maciej Sosna obtained his MSc in chemistry in 2000 from University of Wroclaw, Poland. Currently he is studying for a PhD in the School of Chemistry at the University of Southampton. His work is in the field of micro-electrode sensors for in situ environmental monitoring of dissolved oxygen and is done in collaboration with the National Oceanography Centre in Southampton.

Guy Denuault received his undergraduate training in France then joined the Southampton Electrochemistry Group (UK) and obtained his PhD in 1989. After a postdoctoral position at the University of Texas at Austin, he returned to Southampton as an EPSRC Advanced Research Fellow. He is now a senior lecturer in the Electrochemistry and Surface Science Group. His research focuses on microelectrodes, scanning electrochemical microscopy (SECM) and numerical simulation of electrode reactions. He has been involved for many years with the organisation and delivery of the Southampton Electrochemistry Summer School “Instrumental Methods in Electrochemistry”.

Robin W. Pascal joined the Applied Physics Group at the Institute of Oceanographic Sciences, Wornley, UK in 1979 and followed the Institute to Southampton. His interests include meteorology and air sea interaction and the development of sensors and systems for the direct measurement of wind stress and air–sea heat and water fluxes.

Ralf D. Prien obtained his physics degree (Dipl.-Phys.) from Christian-Albrechts-Universität Kiel, Germany in 1991 and his PhD (Dr. rer.-nat.) in 1999 from the same university. From 1999 to 2005 he worked in the Ocean Engineering Division of the National Oceanography Centre, Southampton, UK on oceanographic sensor development. Since 2005 he works in the Marine Chemistry Department of the Institut für Ostseeforschung Warnemünde, Germany, where he continues his work on oceanographic in situ sensors.

Matt Mowlem obtained his MEng (Aeronautics and Astronautics) and PhD (2002) from the University of Southampton. He is head of the sensor development group within the National Marine Facilities Division at the National Oceanography Centre, Southampton. His interests include in situ optical and electrochemical sensors, microfluidic devices and autonomous vehicles.