Response Characteristics of Two Oxygen Sensors for Oceanic CTDs

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ABSTRACT

Response characteristics of a microhole potentiostatic oxygen sensor and a Beckman membrane oxygen sensor were measured in a laboratory over temperatures ranging from 1° to 21°C. The response term τ of the microhole sensor changed 1.7-fold over this temperature range, and τ of the membrane sensor changed 1.6-fold. For the microhole sensor, the effect of temperature on τ can be modeled as $\ln\tau = -6.5 + 1618T^{-1}$. For the membrane sensor the temperature effect on τ can be modeled as $\ln\tau = -5.8 + 2116T^{-1}$, where T is temperature in kelvins.

1. Introduction

A new type of oxygen sensor for profiling CTDs, the microhole potentiostatic oxygen sensor (POS) was designed and tested in the field (Atkinson et al. 1994; Thomas and Atkinson 1995). The POS has no membrane and employs three electrodes: a cathode, an anode, and a Ag/AgCl reference. The cathode is composed of a 1000 carbon fibers. The tips of the cathodes are plated with platinum and recessed 50 μm within an epoxy microhole structure (Atkinson et al. 1994). The rate-limiting step for the reduction of oxygen at the cathode surface is diffusion of oxygen through the 50-μm-deep microholes. An estimate of response time at 20°C is the timescale to diffuse through this length or 1.2 s [Morita and Shimizo 1989; $L^2/D = (50 \times 10^{-6}\ \mathrm{m})^2/2 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$]. In contrast, a Beckman membrane oxygen sensor (MOS) commonly used on profiling CTDs is reported to have a 63% response time of 2–5 s (Sea-Bird data sheet on Beckman sensors).

In this paper we verify the response characteristics of both a POS and MOS in a common experimental situation. In addition, we quantify the effect of temperature on the response characteristics of these two sensors. Understanding how temperature affects response is important for improving calibrations of oxygen sensors. The algorithm commonly used for calibrating CTD casts assumes a response term (τ) that is not affected by temperature (Owens and Millard 1985). Effects of temperature on diffusivity of oxygen (D) through water or through membranes can be estimated by an activation energy for diffusion,

$$D = D_0 e^{-E/RT}, \tag{1}$$

where E is the activation energy for diffusion (cal mol^{-1}), R is the gas constant (1.987 cal K^{-1} mol^{-1}), and T is temperature (K) (Greene et al. 1970). Thus as D increases with temperature, τ decreases. Our data indicate that activation energies for both sensors are approximately 4000–5000 cal mol^{-1}. Therefore, taking the ratio of D at 2° and 21°C, the change in τ over this temperature range should be between 1.6- and 1.8-fold.

2. Materials and methods

To determine the response of the two oxygen sensors to step changes in oxygen, each sensor was connected to two reservoirs of sea water. One reservoir was left exposed to air so that oxygen concentration was high (near 200 μM O_2). The oxygen concentration in the other reservoir was kept low (near 35 μM O_2) by periodically bubbling nitrogen into the water. Water was pumped through 0.5-in. Tygon tubing and past the sensor at 100 mL s^{-1} (Reynolds number of 6000–10 000) with a Sea-Bird pump (model SBE-5). The two reservoirs were separated by a three-way stop cock so that sea water with either high or low concentrations of oxygen could be pumped past the sensor. Water was not recirculated. Both POS and MOS were enclosed in ducts. The duct for the POS was a straight tube, and the duct for the MOS was cone shaped (Sea-Bird mounting for Beckman sensors). The entire assemblage was submerged in a controlled temperature bath so

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that all equipment used in the experiment was kept at the same temperature. This also ensured that internal and external temperatures for the MOS sensor were matched. Experiments on the two sensors were done separately.

Data from each sensor were collected at 24 Hz by a CTD (SBE-09) interfaced with a deck box (SBE-31) and recorded on a computer. The above procedure was repeated after bringing the temperature bath to near 1°, 4°, 6°, 9°, 12°, 13°, 16°, and 21°C for the POS and to near 0°, 2°, 7°, 13°, 16°, and 21°C for the MOS. All output of a run was normalized to the range in output of that run. At a fixed temperature and pressure, as in these experiment, these normalized data are directly proportional to oxygen concentration. Because change in response time τ is related to changes in diffusivity of oxygen, and this diffusivity is affected by temperature [Eq. (1)], we modeled the effect of temperature on τ as a natural log function, $\ln\tau = (E/R)T^{-1}$, where T is in kelvins.

The response times for both sensors were determined by calculation ("calculated") and by iteration ("iterated"). Values of τ were determined by iteration to confirm and improve those determined by calculation. Response times were calculated by assuming the rate of change of the output signal can be modeled as a first-order equation. Using the techniques of Fozdar et al. (1985), a least squares regression of the best fit of $\ln Y_k'$ versus time yields τ:

$$Y_k' = \frac{Y_f - Y_t}{Y_f - Y_i}, \qquad (2)$$

where Y_t is output at time t, Y_i is initial output, Y_f is the final output, and the slope of the regression is $-1/\tau$. Initial output Y_i for each run was chosen as the point where the signal began to deviate from the steady-state value, and Y_f was chosen as 63% of the final value of the output for the calculation of τ. To illustrate the entire response of the sensors we also calculated Y_k' with Y_f chosen as 99% of the final value.

To determine values of τ by iteration, iterated values of τ were applied to the measured output (mo) to create a corrected output (co):

$$\text{co} = \text{mo} + \tau\,(d\text{mo}/ds), \qquad (3)$$

where s is seconds. The selected τ was the highest value of τ that sharpened the corrected output, without causing corrected output to exceed the final value of measured output (e.g., Vollmer 1991). The output of the MOS was averaged to 4 Hz when values of τ were selected by iteration, because the response of this sensor was slow relative to the sampling rate thus creating spikes in estimates of $d\text{mo}/ds$.

3. Results

a. Potentiostatic oxygen sensor

The response of this sensor, illustrated as Y_k' versus time, is shown in Fig. 1. Calculated values of τ ranged from 0.32 to 1.38 s (Fig. 2a, Table 1). Values for increasing steps of oxygen were lower than those for decreasing steps (paired t test; $T = 4.6$, df = 7, $p < 0.003$; Fig. 2a). The mean values of τ changed 1.3-fold between 1.3° and 21.5°C (Table 1). There was no significant correlation between temperature and calculated values of τ (Fig. 2a).

Values of τ that were determined by iteration ranged from 0.26 to 1.04 s (Fig. 2b, Table 1). Values for increasing steps of oxygen were lower than those for decreasing steps (paired t test; $T = -5.7$, df = 7, $p < 0.001$; Fig. 2b). The mean values of τ changed 1.7-fold between 1.3° and 21.5°C (Table 1). The best fit for the effect of temperature on τ is $\ln\tau = -6.5 + 1618T^{-1}$ ($r^2 = 0.14$, $n = 40$, $F = 8.8$, $p < 0.005$). The slope of this fit is E/R in Eq. (1).

b. Membrane oxygen sensor

The response of this sensor, illustrated as Y_k' versus time, is shown in Fig. 1. Calculated values of τ ranged

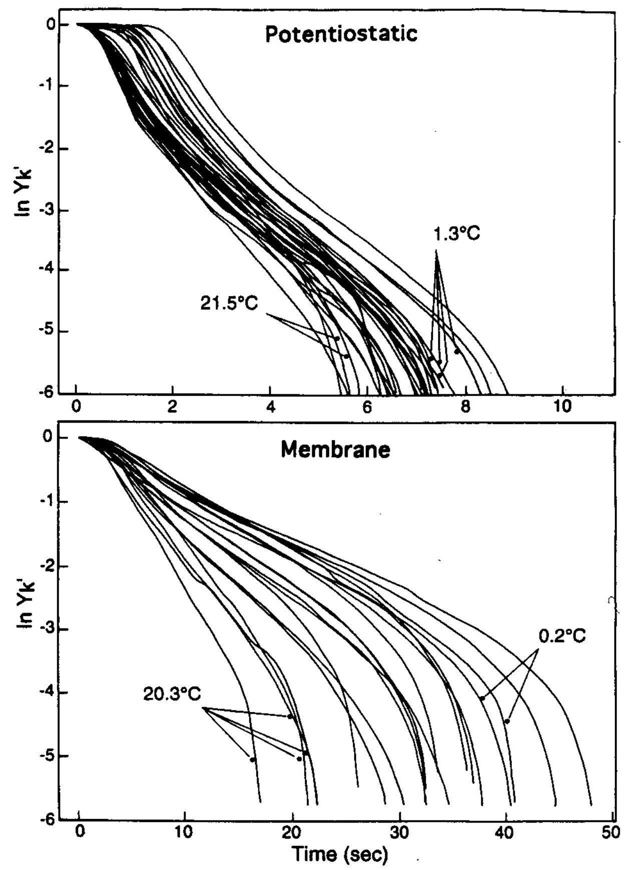

FIG. 1. The response of potentiostatic (POS) and membrane (MOS) oxygen sensors illustrated as ln Y_k versus time, where $Y_k = (Y_f - Y_t)(Y_f - Y_i)^{-1}$. Here Y_f was chosen as 99% of the final value to illustrate the entire response. Note that the response of the MOS is about five times slower than the POS.

TABLE 1. Mean and range of iterated and calculated values of τ for a microhole potentiostatic oxygen sensor (POS) and a membrane oxygen sensor (MOS). The time required to reach a response time of x% can be calculated as $t = -\tau \ln(100 - x)/100$, where t is time (s).

Temperature (°C)	Iterated τ (s)			Calculated τ (s)		
	Mean	Range	n	Mean	Range	n
POS						
1.0–1.6	0.71	0.40–1.04	3	0.49	0.38–0.54	3
3.6–3.8	0.51	0.43–0.80	5	0.42	0.40–0.56	5
5.9–6.3	0.57	0.47–0.81	5	0.45	0.37–0.68	4
8.2–8.8	0.43	0.35–0.53	6	0.40	0.35–0.48	5
11.3–11.9	0.42	0.34–0.53	5	0.58	0.32–1.02	5
12.3–13.7	0.49	0.34–0.71	5	0.57	0.38–1.38	5
15.2–16.2	0.43	0.33–0.57	6	0.53	0.37–0.87	6
21.5–21.6	0.41	0.26–0.70	5	0.37	0.32–0.40	5
MOS						
0.1–0.3	6.5	5.7–7.1	5	3.5	3.0–4.4	5
2.0–2.1	6.7	5.9–8.3	3	2.9	2.6–3.5	3
7.0–7.8	5.6	5.0–6.1	4	2.7	2.4–3.0	4
13.3–13.4	4.9	4.5–5.1	4	2.2	2.1–2.3	4
16.2–16.5	4.3	4.0–4.7	5	2.0	1.8–2.1	5
19.9–20.7	4.1	3.8–4.9	4	1.8	1.7–2.0	4

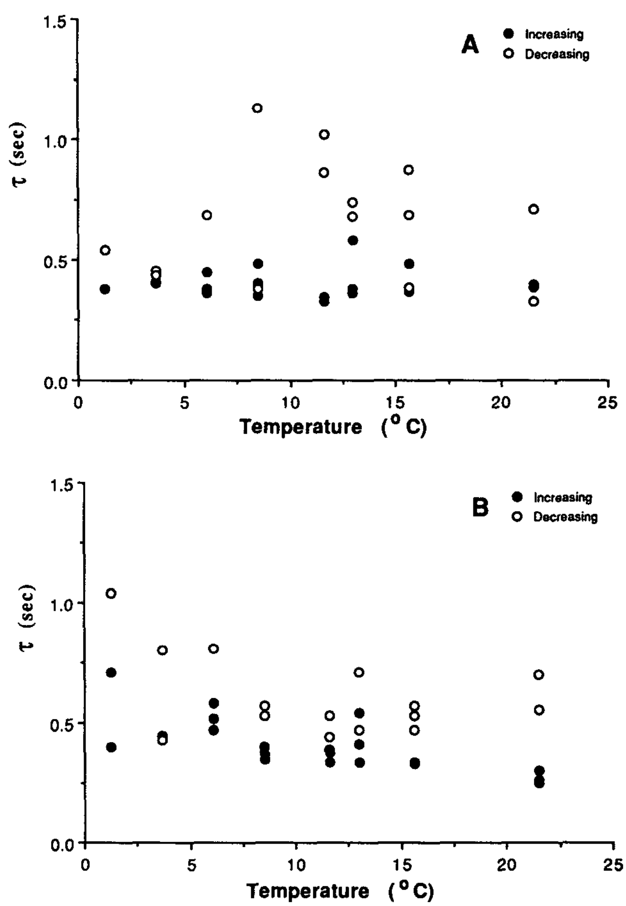

FIG. 2. Calculated (a) and iterated values (b) of the response term τ for the microhole POS. Note τ's for increasing oxygen steps are generally less than those for decreasing steps.

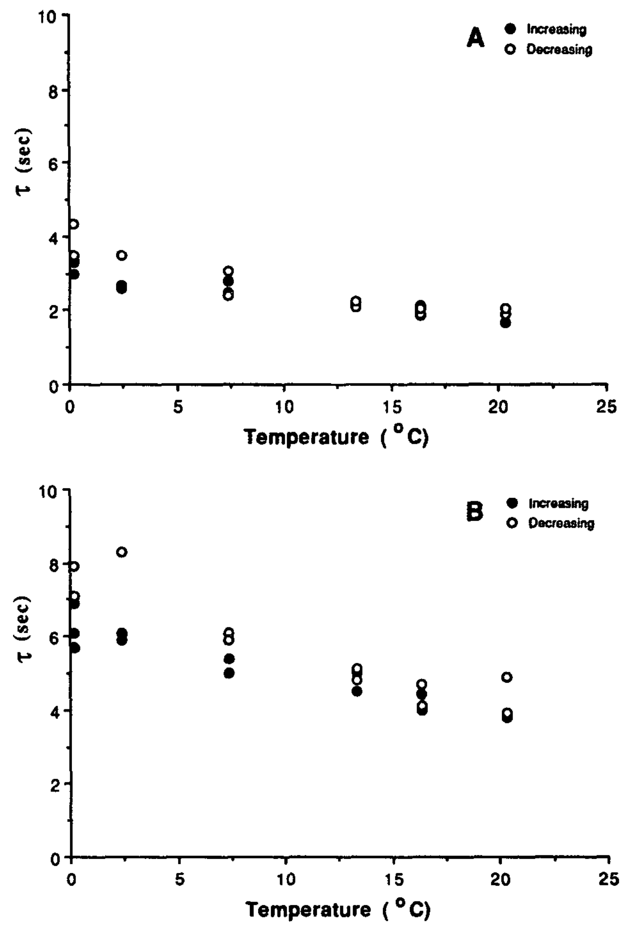

FIG. 3. Calculated (a) and iterated values (b) of the response term τ for the MOS. Note τ's for increasing oxygen steps are generally less than those for decreasing steps.

from 1.7 to 4.4 s (Fig. 3a, Table 1). Values for increasing steps of oxygen were lower than those for decreasing steps but not significantly lower (paired t test; $t = 2.1$, df = 7, $p = 0.09$; Fig. 3a). The mean values of τ changed 1.9-fold between 0.2° and 20.3°C. The best fit for the effect of temperature on t is $\ln\tau = -7.9 + 2505T^{-1}$, where T is kelvins ($r^2 = 0.84$, $n = 25$, $F = 125$, $p < 0.001$).

Values of τ that were determined by iteration ranged from 3.8 to 8.3 s (Fig. 3b, Table 1). Values for increasing steps of oxygen were lower than those for decreasing steps (paired t test; $T = 2.6$, df = 5, $p = 0.023$; Fig. 2d). The mean value of τ changed 1.6-fold between 0.2° and 20.3°C (Table 1). The best fit for the effect of temperature on τ is $\ln\tau = -5.8 + 2116T^{-1}$ ($r^2 = 0.79$, $n = 25$, $F = 90$, $p < 0.001$).

4. Discussion

It was unexpected that response times of the sensors to increasing steps of oxygen were faster than to decreasing steps of oxygen. This difference in response with the direction of the oxygen step accounts for much of the variability in our data at a given temperature. This creates error in our overall estimate of the effects of temperature on τ (Fig. 2). For both sensors the r^2 of the regression of $\ln\tau = \alpha T^{-1}$ improved when increasing and decreasing steps were treated separately. We offer the following explanation for the faster response of both sensors to increasing steps of oxygen than to decreasing steps. The epoxy and plastic materials that form walls near the cathode of the sensor absorb oxygen. When oxygen concentrations are changed from high to low, there is residual oxygen in these materials. The lag in response is the result of oxygen diffusing from these materials into the diffusion path. This oxygen must be depleted before the sensor responds to the new lowered concentration of oxygen.

Iterated and calculated values of τ for both POS and MOS were within a factor of 2. This gives us some confidence that calculated values are mostly correct. However, when calculated τ's are used in Eq. (3) to sharpen the signal, some of the τ's for the POS are too large and cause overshooting of the final value of measured output. For the MOS calculated values are too small. Thus, the signal is not sharpened to the greatest extent possible. Therefore, in general we believe that iterated values of τ are the best approximation of the true response of these sensors.

We have clearly shown an expected temperature effect on response time that is consistent with our understanding of the operation of these sensors. The response time is controlled by the rate of diffusion of oxygen through the membrane for the MOS and through the diffusion channels for the POS. The effect of temperature on response time is directly related to the activation energy for diffusion. Therefore the effect of temperature on the response time of an oxygen sensor will be dependent on the activation energy of the diffusive barrier employed on that sensor.

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