Technical report

Solid-state electrolyte sensors for rebreather applications: a preliminary investigation

Arne Sieber, Rainer Baumann, Stefanos Fasoulas and Anatol Krozer

Key words
Rebreathers/closed circuit, oxygen, carbon dioxide, transducer, capnography, helium, trimix

Abstract
(Sieber A, Baumann R, Fasoulas S, Krozer A. Solid-state electrolyte sensors for rebreather applications: a preliminary investigation. *Diving and Hyperbaric Medicine*. 2011;41(2):90-6.)
Introduction: Recently developed prototypes of zirconium dioxide and NASICON-based micro solid-state electrolyte oxygen (O_2) and carbon dioxide (CO_2) sensors were tested for their potential suitability in rebreathers. The O_2 sensor has a quasi-indefinite lifetime, whilst that of the CO_2 sensor is approximately 700 h. This is a preliminary report of a new technological application.
Methods: The O_2 sensor was tested in a small pressure chamber to a partial pressure of oxygen (PO_2) of 405 kPa (4 bar). The CO_2 sensor was tested up to 10 kPa CO_2. The response times to a step change of pressure were measured, and cross-sensitivity for helium tested using trimix. A rebreather mouthpiece was modified so that breath-by-breath gas recordings could be observed. Power consumption to heat the sensors was measured.
Results: The O_2 sensor demonstrated non-linearity, particularly above 101.3 kPa (1 bar) PO_2, whereas the output of the CO_2 sensor showed an inverse logarithmic relationship. Cross-sensitivity to helium was observed. The mean t90 response times were 90 (SD 10) ms for the O_2 sensor, and 100 (SD 10) ms for the CO_2 sensor. Breath-by-breath recordings showed slight damping of the CO_2 trace due to electronic filtering. Power consumption was 1.5–2 W per sensor.
Conclusions: The fast response times would allow accurate breath-by-breath measurement. Even though the O_2 sensor has a non-linear response, measurement is possible using multi-point calibration. Further design is necessary to allow trimix to be used as the diluent. A major disadvantage is the high power consumption needed to heat the sensors to high temperatures.

Introduction

GAS MONITORING IN CLOSED-CIRCUIT REBREATHERS

While in open-circuit scuba diving, exhaled gas is usually vented into the water, in a rebreather it is returned to a counterlung, carbon dioxide (CO_2) is removed in a 'scrubber' and metabolised oxygen (O_2) is added from the supply tank. Information about the various types of rebreathers available can be found elsewhere.[1,2] In a closed-circuit rebreather (CCR), the partial pressure of O_2 (PO_2) is usually kept at a constant level and only metabolised O_2 is replaced with fresh O_2 from the supply tank.[3,4] Oxygen is diluted in the breathing circuit with nitrogen or helium, or a combination of these gases. To maintain the PO_2 at a constant level, a control loop is needed. Therefore, electrochemical oxygen transducers, whose output signals are proportional to the PO_2, are used as sensing elements. In a manually controlled rebreather, the diver reads the PO_2 from a display, then, if necessary, adds O_2 manually and/or, as in one model, adjusts the O_2 injection needle valve. In an electronically controlled rebreather, this control task is usually performed by a micro-controller and a solenoid valve.

CCRs have many advantages, such as:

- high gas efficiency, close to 100%;
- stealth (silent, bubble-free diving);
- warm, humid breathing gas;
- extended diving time;
- reduced decompression obligations due to optimised gas mixtures and decompression mixtures.

Risks and accidents associated with rebreathers have been discussed in detail elsewhere.[5] The most commonly identified systems failures that cause fatalities are:

- PO_2 outside of life-sustaining limits;
- high CO_2 levels.

In current rebreathers, O_2 is measured using galvanic sensors. The core element of this transducer is an electrochemical cell (fuel cell) consisting of two electrodes of dissimilar metals (cathode – a noble metal behind a diffusion barrier, made usually of Teflon; anode – lead) in contact with a liquid or semi-solid basic electrolyte, usually potassium hydroxide. The transducer output is linear in the range up to 203 kPa (2 bar) PO_2 with a slope of 40–70 mV bar^{-1}. The most common and, for the diver, most dangerous failure mode of a PO_2 transducer is an incorrect electrical output for a given PO_2.

In order to achieve maximum safety in the case of a PO_2 transducer failure, two main strategies are used:

- redundancy, using several transducers together with a voting logic;
- transducer validation.[6,7]

As well as having several failure modes, current PO_2 transducers also face disadvantages such as:

- short lifetime (< 18 months);
- relatively slow and temperature-dependent response (t90 typically approximately 6 s at room temperature).

High CO_2 levels may be due to scrubber failure from various causes or check valve/direction valve failures that lead to 'pendulum breathing', in which the breathing gas no longer passes through the scrubber. Another important physiological rather than technical cause of hypercapnia is hypoventilation, especially at depth.[8] When CO_2 is chemically absorbed in the scrubber, heat and water are produced as by-products. Temperature at several points in the scrubber can thus be used for monitoring the scrubber and predicting its life-time.[9]

Although these technologies have been successfully implemented already, they provide feedback on the activity of the scrubber only, not on the inspired CO_2. CO_2 measurement is usually performed using optical sensors. CO_2 shows strong (infrared) light absorption at 4.26 μm and 15 μm wavelengths. Most commercial optical CO_2 transducers are based on Beer-Lambert light absorption at 4.26 μm. They have fast response times, a quasi-indefinite lifetime and are inexpensive, and until recently have not been used in rebreathers. In a rebreather, where the humidity in the loop is approximately 100%, condensation may lead to the failure of optical transducers, as any additional absorption in the optical measurement path leads to unreliable readings.

A proof of concept of a gaseous CO_2 monitor for rebreathers based on an optical CO_2 transducer (Gas Sensing Solutions, UK) was first presented by Amphilogic Ltd (UK) in 2008 at the Birmingham dive show. Recently, a CO_2 transducer for rebreather applications, based on the same transducer module has been launched.[10] In order to overcome the problem with high humidity, hydrophobic membranes and a sponge are mounted in front of the transducer. However, such measures are likely to lead to increased response times. Another approach is based on an optical CO_2 transducer at the end of the exhale hose. A preliminary study of the performance of this CO_2 transducer, particularly in relationship to its positioning in the rebreather circuit was reported recently in this journal.[11]

SOLID-STATE TRANSDUCERS FOR GAS MONITORING

An alternative to liquid electrolyte transducers is solid-state technology, based mainly on the ionic conductivity of ceramic materials.[12,13] This technology has been used for many years in cars for combustion control (Lambda probe). At present, only yttrium oxide-doped zirconium dioxide (Zirconia, YDZ) is used in commercial sensors as a conducting solid-state electrolyte. Conductivity in YDZ requires high temperatures. Therefore, the sensor is heated by an electrical resistance to reach an operational temperature of about 650^{O}C. The O_2 transducers typically used in cars are not applicable for a rebreather, mainly because of their power consumption and size; they also require a reference chamber. In automotive applications, ambient air is taken as a reference, which is, of course, impossible for an underwater breathing apparatus. Micro manufacturing allows miniaturisation of such transducers. An overview of micro solid-state gas sensors can be found elsewhere.[14] A suitable ionic conductor for a CO_2 sensor is sodium super-ionic conductor (NASICON).

Recently, micro solid-state sensors have been developed in Germany for O_2 measurement in low earth orbit and tested in the International Space Station (ISS). These are based on the amperometric principle, where the electrical current is proportional to PO_2 flow through the sensor membrane when the O_2 is 'pumped' from one electrode to the other by an applied voltage. The reaction proceeds in several steps. Firstly, molecular O_2 is transformed to oxygen ions at the cathode. Then these ions migrate through the solid electrolyte towards the anode, where they recombine again into O_2 molecules. In addition, a diffusion barrier limits the O_2 flux to the cathode. If the flux limitation is high enough, the PO_2 at the cathode is very low. In this particular case, the measured current is limited by the diffusion of O_2 to the cathode and, therefore, a linear dependence on the ambient PO_2 is achieved as long as 'crowding' of O_2 at the anode is avoided. Unlike the typical Lambda probe in a car, these types of sensors do not require a reference but instead require an efficient O_2 clean up from the anode.

Based on the test results from the ISS, a new project was started to develop micro solid-state O_2 and CO_2 transducers for respiratory analysis using this sensor technology. This is supported by the European Space Agency within the framework of the Microgravity Application Promotion Program (MAP Project No. AO-99-058; ESTEC Contract No. 14350/01/NL/SH). The focus for these investigations is to design and test a new miniaturised transducer system that enables simultaneous in-situ measurement of O_2, CO_2 and volume/mass gas flow rates. This allows for direct in-situ measurements inside the mask during cardio-respiratory studies of astronauts, athletes and medical patients. Since the in-situ measurements are performed with the transducer inside the mask, one measures these parameters in the main gas stream, avoiding any of the problems of side-stream measurement. The main characteristics of the transducers are listed in Table 1.

The aim of the present investigation was to validate the

Table 1
Specifications of the micro solid-state O_2 and CO_2 sensors

Oxygen
- Yttria-doped Zirconia (YDZ)
- Amperometric principle
- Operational temperature approx. 650°C (high temperature is required for linearity)
- 1.8 W power supply (1 W supply in principle possible, but more difficult to fabricate)
- Accuracy of < 2% volume at ambient pressure should be possible after 3 s heating
- Accuracy of +/- 0.1% at ambient pressure after 3–4 min
- Quasi-indefinite lifetime

Carbon dioxide
- NASICON-based
- Potentiometric transducer principle (with a solid reference), thus the electromotive force (EMF) is measured
- Operational temperature approximately 550°C
- 1.8 W power supply
- Operational lifetime approx. 700 h

performance of the micro solid-state sensors in conditions similar to those existing in a rebreather (PO_2 15–203 kPa, PCO_2 0–6 kPa). The response times of the transducers were of considerable interest as, due to their small size, they can be integrated into a mouthpiece, which theoretically allows breath-by-breath analysis of the inhaled and exhaled gases. Of particular interest was performance of the present transducer design when used in conjunction with the gas mixtures characteristic for the diving environment, i.e., O_2 in nitrogen (N_2) and helium (He)-N_2 admixtures.

Methods

A test bench, which included a small pressure chamber (approximately 10 cm³ volume) that can be pressurised up to 10 bar (Figure 1), was designed for measuring the performance of the solid-state sensors. Gas was supplied to the chamber via an adjustable needle valve from a 4-L cylinder. The supply pressure was reduced to 8 bar over ambient with a commercially available first stage regulator [DS4, Apeks]. A mechanical gauge and a calibrated absolute pressure transducer [MPX5700AP, Motorola] were used to measure the pressure inside the chamber. A pressure regulator [Porter USA] kept the pressure at a manually selectable level (0–4 bar above ambient). Alternatively, a quarter-turn shut-off valve could be mounted instead of the pressure regulator. In the closed position, the pressure inside the chamber will rise to the output pressure of the first stage regulator; opening the valve leads to a sudden loss of pressure, allowing measurement of the response time of the sensors to a step change in pressure. All components are either oil/grease free or are assembled using oxygen-compatible grease.

The O_2 sensor output was loaded with a 1 kΩ resistor. The voltage was then amplified with an operational amplifier (AD8630, Analog Devices). The CO_2 sensor signal was buffered with a precision operational amplifier (AD8601, Analog Devices) with a very low input bias current, typically 0.2 pA, making it the ideal choice for signal conditioning of a CO_2 sensor with a high output impedance. The conditioned sensor signals and the output signal of the pressure transducer were sampled with a 12-bit data acquisition card (USB-6008, National Instruments).

The solid-state sensors were heated by a printed platinum resistor (approximately 3 Ω at room temperature and 9 Ω at 700°C). For temperature control and transducer readout, custom electronics were developed, based on an 8-bit microprocessor (ATXmega16A4, Atmel). The temperature control programme essentially measures the heating current with the internal AD converter of the microprocessor, calculates the resistance and then sets the pulse-width modulation based on a proportional integral algorithm (PI control). Another two analog inputs of the microprocessor are used to sample the signal from the O_2 and the CO_2 sensors. These data, together with the heater currents and the calculated resistances, are transmitted via a serial interface to a PC at a sampling rate of 50 Hz. Data acquisition, conditioning and visualisation were performed using the software package Lab View™ 8.5 (National Instruments, Austin, Texas, USA).

EXPERIMENTAL PROCEDURES

Four separate tests were conducted. First, the O_2 sensor was installed in the test chamber and the gas flow was set to 0.5 L min^{-1} STPD. The chamber was gradually pressurised with O_2 in 0.1 bar steps from 1 to 4 bar absolute pressure. For O_2 values below 1 bar (101.3 kPa) the chamber was pressurised with air. To assess He cross interference, the O_2 sensor was exposed to trimix 21/50 from 1 bar to 5 bar absolute pressure.

Figure 1
Test bench for hyperbaric characterisation of micro solid-state O_2 and CO_2 sensors

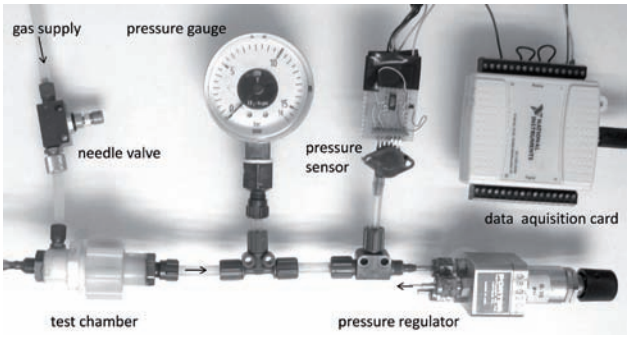
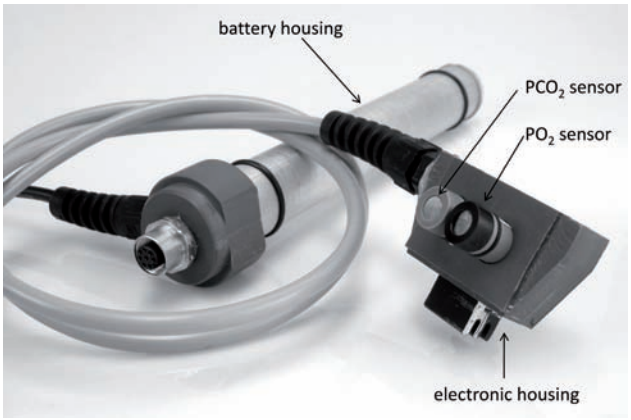


Figure 2
PO_2 and PCO_2 solid-state transducer module, electronics and rechargeable battery pack



The heating power was about 2.5–2.6 W.

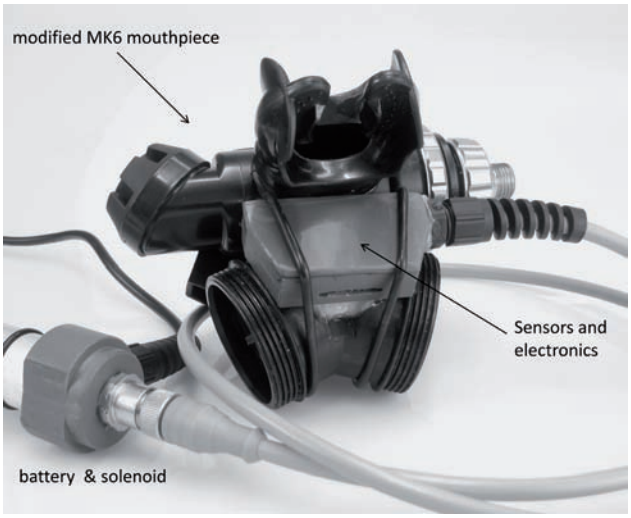
For response-time measurement, the pressure regulator was substituted with the quarter-turn shut-off valve and the chamber was pressurised with air at a gas flow of 0.1 L min^{-1} STPD. After reaching 7 bar, the shut-off valve was opened leading to a rapid decrease in pressure. Pressure signals and transducer signals were recorded and t90 was estimated using Microsoft Excel®.

Assessment of the signal response of the CO_2 sensor to CO_2 partial pressures (PCO_2) from 0–10 kPa was performed by gradually increasing the pressure inside the chamber using an air/CO_2 mixture with an FCO_2 of 1%. The CO_2 sensor is a potentiometric transducer, thus the output is logarithmic (Nernst equation). The response time of the sensor was measured in the same manner as for the O_2 sensor but using the 1% CO_2 gas mixture.

For the third test, a small module, measuring 22x10x5 mm and containing CO_2 and O_2 sensors and the required electronics, was built into a custom-made PVC housing filled with silicone gel. As well as transducer control and readout, it was also equipped with a solenoid controller, a display interface and a serial output for real-time data transmission to a PC (Figure 2).

A commercially available rebreather mouthpiece (Mk6, Poseidon, Sweden) was modified with a support that allowed fitting of the transducer module onto the mouthpiece such that the sensors sat between the mushroom valves (Figure 3). The module was connected via a water- and pressure-proof cable to the battery housing. It was also possible to install into the head of the battery housing a micro-solenoid for O_2 partial pressure (PO_2) control. As reference, a commercially available main-stream infrared CO_2 analyser (IRMA, Phasein, Sweden) was fitted between the bite and the rebreather mouthpiece.

Figure 3
Transducer module fitted onto a modified rebreather mouthpiece



In a final study to measure breath-by-breath PO_2 and PCO_2, a subject (35-year-old male) breathed through the rebreather mouthpiece. In all studies, repeat observations were made. The CO_2 transducer was two-point calibrated with air (assuming 350 ppm CO_2) and with air containing 1% CO_2.

Results

Figure 4 illustrates the results of the O_2 sensor characterisation with 100% O_2, air and Trimix 21/50. As the sensor elements studied were prototypes only mean values are shown at this

Figure 4
Illustrative characterisation of the O_2 sensor with O_2, air and trimix 21/50

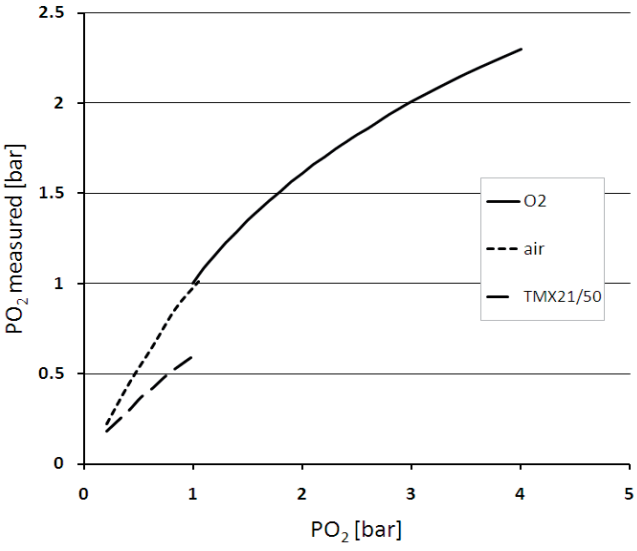


Figure 5
Characterisation of the CO_2 sensor from 0.01 to 0.1 bar PCO_2 with a 1% CO_2/air mixture

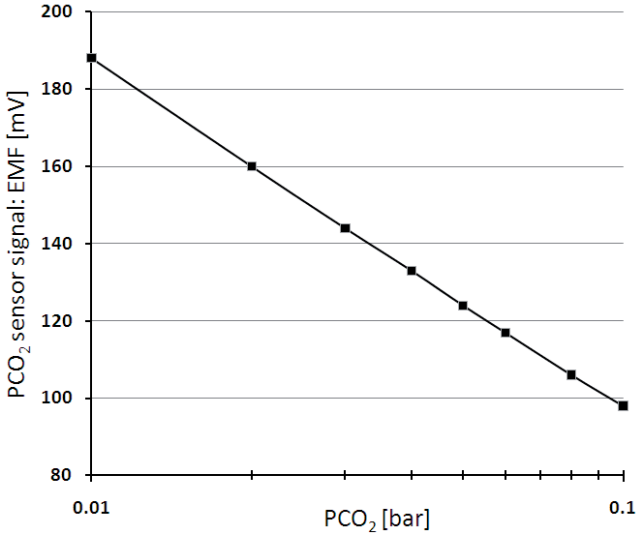
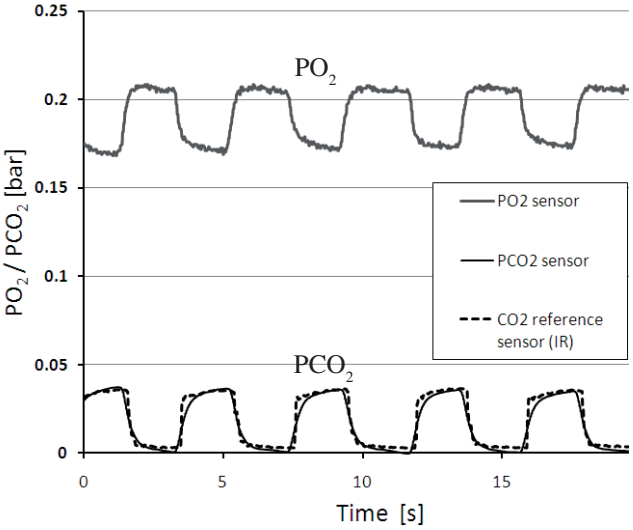


Figure 6
Sample breath-by-breath O_2 and CO_2 recording from the transducer module in the rebreather mouthpiece; measurements from mainstream CO_2 monitor also shown



stage. The sensor signal is non-linear, particularly at a PO_2 above 1 bar. The heating power was fairly constant with 1.65 W at 1 bar and 1.75 W at 4 bar chamber pressure. Using the same calibration factor as in the previous test, the sensor output using trimix was lower than expected. Instead of 0.21 bar O_2 at a chamber pressure of 1 bar, the observed PO_2 was 0.18 bar. At 5 bar chamber pressure, equal to a PO_2 of 1.05 bar, the observed PO_2 was only 0.65 bar. In comparison to the previous tests with 100% O_2, the required heating power was increased by approximately 40%.

Because the PCO_2 transducer is based on a potentiometric principle, the EMF produced is inversely related to PCO_2 in a logarithmic fashion, shown as a semi-log plot in Figure 5. The required heating power was 1.7 W and was fairly constant from 1 to 10 bar absolute pressure. The sensitivity was found to be -90 mV per decade (EMF @ 0.1 bar – EMF @ 0.01 bar PCO_2).

Using the quarter-turn valve, the pressure inside the chamber fell from 7 to 1 bar within approximately 25 ms. The mean t90 response time of the O_2 transducer was 90 (SD 10) ms, and that of the CO_2 transducer was 100 (SD 10) ms (n = 10).

Figure 6 shows an example recording of the breath-by-breath PO_2 and PCO_2 outputs and that of the reference CO_2 monitor. The average end-tidal CO_2 difference between the solid-state PCO_2 transducer and the infrared reference transducer over a 3 min recording period was found to be 0.26 (0.06) kPa.

Discussion

The recently developed prototypes of solid-state O_2 and CO_2 sensors seem to be suitable for applications in an O_2/N_2 rebreather. The main advantages are:

- very long lifetime;
- high accuracy;
- mechanically robust;
- insensitive to moisture/humidity (heated up to 600^{o}C);
- very fast response time, that allows assessment of PO_2 and PCO_2 values in inhaled and exhaled gas.

The main disadvantages are a high power consumption and non-linearity.

The current sensor prototype was developed for O_2 measurements below 1 bar PO_2. Above 1 bar PO_2, the sensor is non-linear, and so requires multi-point calibration to enable accurate measurements. In comparison to traditional wet-electrochemistry-based O_2 transducers containing a consumable lead anode, the micro solid-state technology is non-consuming and theoretically the signal response of the sensor does not change over time. Thus, a one-time factory calibration is conceivable. Even though this would obviate the need for pre-dive calibration, we believe that a pre-dive calibration with normobaric O_2 is a necessary safety measure to validate transducer function.

Further development will include optimisation of the diffusion layer in terms of thickness and density to improve linearity up to a PO_2 of 2 bar. An alternative approach to improving linearity might be three-electrode configuration together with a potentiostat, which is an electronic circuit used to maintain the voltage on one electrode at a defined level by using a third electrode, usually referred to as the reference electrode. Long-term aging effects caused by thermal stress (because of fast heating and cooling

of the transducer elements) were not investigated in this preliminary study.

The typical heating power required for a sensor is 1.7 W. Even with He in the diluent, no higher values than 2.5 W heating power were recorded. A standard 3.3 V, 2000 mA h^{-1}, rechargeable battery would allow operation of a single transducer for approximately 3 h with air as the diluent, which is sufficient for a rebreather for recreational purposes. Promising approaches to reduce the required heating power are based on further miniaturisation of the sensor element, the use of different ionic conductors that work at lower temperatures and smart system design with an emphasis on isolation and packaging of several transducers in one device.[15,16]

The PO_2 transducer in its current version does not appear suitable for use in a rebreather with He gas mixtures as the addition of He to the diluent decreased the sensitivity of the sensor. We believe this is due to an increased temperature gradient that is created by the presence of He. He has a much higher heat conductivity than air (or O_2 or N_2), which causes an increased heat loss at the sensor surface. To compensate for this, more power is necessary. The heating resistor, which is also used for sensing the sensor temperature, is located in the first layer above the sensor substrate. The increased heating power required results in a larger temperature gradient across the sensor. The diffusion layer, which is the current-limiting component, is distant from the resistor layer and, because of the temperature gradient, is most likely colder when He is used compared to air, which then leads to a reduced output signal in the presence of He. Possible solutions could be the integration of a temperature-sensing element in front of the sensor surface or measures for calibration of the transducers for different He fractions.

Figure 6 shows the results of the comparison of the PCO_2 transducer and the reference infrared-based CO_2 transducer. Even though the O_2 and CO_2 sensors have a short t90 response time and can be used for breath-to-breath gas analysis (Figure 6), the signal response of the solid-state PCO_2 transducer is slower than that of the reference monitor. This is because of an internal low-pass filter in the electronics. The filter frequency will be changed in the next hardware revision to allow full exploitation of the sensor's capabilities. It should be noted, that a CO_2 calibration using a precision gas with a higher CO_2 content might lead to more accurate values. Whether such a calibration can be carried out as a one-time factory calibration, or has to be performed at regular intervals by the user or a service centre, has yet to be assessed by long-term studies.

Conclusions

This paper presents preliminary data describing the characteristics of micro solid-state sensors for O_2 and CO_2 monitoring being developed for gas monitoring in diving rebreathers. These data confirm the potential successful application of this technology. Issues of non-linearity and helium cross-sensitivity require further investigation. Future testing will also address vulnerability of the heated transducers to heat shock and immersion in water, aging effects (especially from thermal stress) and how different breathing patterns influence transducer output on a breath-by-breath basis.

Acknowledgements

This work was partly supported by the FP7-People-IEF-2008 (Marie Curie) action, project nr. 237128.

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Submitted: 07 June 2010
Accepted: 04 April 2011

Arne Sieber, PhD, is a research scientist at IMEGO AB, Göteborg, Sweden.
Rainer Baumann, Dipl Ing, is a doctoral student at the Institute of Aerospace Engineering at the Technical University of Dresden, Germany.
Stefanos Fasoulas, Dr Ing, is Professor at the Institute of Space Systems, University of Stuttgart, Germany.
Anatol Krozer, PhD, is professor and senior scientist at IMEGO AB, Göteborg, Sweden.

Address for correspondence:
Dr Arne Sieber
Arvid Hedvalls Backe 4,
SE-40014 Goeteborg,
Sweden
Phone: *+46-(0)709-151-814*
Fax: *+46-(0)31-750-1801*
E-mail: *<asieber@gmx.at> or*
<arne.sieber@imego.com>