THE FUTURE OF OXYGEN SENSING FOR MILITARY REBREATHERS

Before we can discuss the future of oxygen sensing it is necessary to consider some of the history and technical limitations in order to fully understand the issues facing military divers, identify the solution that both improves operability and diver safety and reduces the through life support burden.

HISTORY

The oxygen sensor was invented in the 1960's. Oxygen sensors were developed as atmospheric pressure devices to measure up to 1 bar partial pressure of oxygen (PPO_2) or 100% oxygen at sea level.

The first use in a rebreather was by Walter Stark in the Electrolung. Development of the Electrolung came about through a chance meeting of John Kanwisher and Walter Stark aboard Ed Link's diving research vessel in the Bahamas in early 1968. Link was trying out his new diver lock-out submarine 'Deep Diver' and had invited along several researchers with relevant interests. Stark was there to do some deep biological collecting and Kanwisher was there to conduct heart rate/respiration measurements on divers using some new acoustical telemetry equipment he had developed. Coincidently they had both been considering the feasibility of a mixed gas Closed Circuit Rebreather (CCRB) using electronic sensors to control the PPO_2. Hence, the Electrolung was born.

In the underwater environment, oxygen sensors have proved to be a useful tool for over 40 years. In the medical industry every life support system; anesthetic machine, ventilator and incubator has at least one sensor and sometimes two. Globally, there are several manufacturers of oxygen sensors.

CONCEPT

While there are several types of oxygen sensor, the one historically suitable for diving applications has been the galvanic fuel cell. This encompasses a 'wet element' and an electronics package. Combined, this makes a partial pressure of oxygen measurement sensor.

As described, the oxygen sensor (or more specifically the oxygen cell) is an electro-chemical device. Possibly the best way to think of it is that it has similarities to a battery. A battery is a complete electro-chemical device and can provide a maximum voltage and current based on its design specification. Over time that output reduces (decays) and eventually falls to zero.

However, unlike the battery, the oxygen cell is initially inactive and requires an additional catalyst (oxygen) to start the chemical reaction and hence produce an electrical output. The time over which the output of an oxygen cell decays is primarily a function of the amount of oxygen it is exposed to.

OPERATING PRINCIPLE

Oxygen (O_2) is a gas. When exposed to the chemical elements within the sensor it produces a reaction. The chemical elements typically found in a typical oxygen cell are:

- Lead (PB) – the anode
- Platinum (PT) – the cathode
- Potassium hydroxide (KOH) – the electrolyte

Oxygen in contact with the cathode is reduced to hydroxyl ions, with a balancing reaction of lead oxidation at the anode. The reaction equations are:

- Cathode $O_2 + 2H_2O + 4e^- \rightarrow 4OH$
- **A**node $2Pb + 4OH^- \rightarrow 2PbO + 2H_2O + 4e^-$
- Overall $O_2 + 2Pb \rightarrow 2PbO$

The result is that oxygen cells generate an electrical current (not a voltage), which is proportional to the rate of oxygen consumption[1]. This current is easily measured by placing a load resistor between the cathode and the anode (the 2 pins on the 'wet element' of an oxygen cell) and measuring the resultant voltage drop across the resistor.

The anode is made from lead but is not solid; it is a collection of small balls of lead compressed into a doughnut. This has the effect of distributing the usage of lead throughout the sensor's life. During the electrochemical reaction, the oxygen converts the lead to lead oxide which in turn generates the electrical current coming out of the sensor.

As the lead is used, the surface area of the anode reduces and therefore the electrical output falls. The use of bonded lead (the lead balls are compressed so they 'stick' together) helps reduce this effect therefore maintaining a fairly constant output until the end of the sensor's life. Although the sensor exhibits a measurable decrease in output until the end of its life, it is not a continuous linear reduction

Most galvanic oxygen sensors use a perforated and convex gold or platinum (or another noble metal) plated sintered steel cathode. The cathode lets the electrolyte through, which keeps the top of the cathode continuously wet (with electrolyte) and ensures minimal internal resistance during the oxygen sensing action. This, combined with the oxidisable lead anode, completes the electrochemical reaction. The sensor's lifetime is a function of the amount of lead remaining in the anode and, as the output remains nearly constant until most of the lead is oxidised, the oxygen sensor's 'end of life' is difficult to predict.

The most common electrolyte used in oxygen sensors is potassium hydroxide (KOH), as lead oxidation is best controlled in an electrolyte with a pH between 10 and 12 (although weak acids can also be used). Henry's Law dictates the speed at which the gases theoretically can pass in and out of the sensor electrolyte.

As lead oxidises the oxide occupies more volume than pure lead, so the combined anode and electrolyte volume inside the oxygen sensor expands. If the sensor is not correctly designed, then the internal pressure can rise and cause the sensor to become inaccurate and it may eventually damage the device. The use of a flexible rear membrane helps equalise the volume.

In a typical rebreather application, a 'Teflon like' solid polymer membrane is used to diffuse the gas into the sensor and a hydrophobic membrane is added to help keep the Teflon membrane clear of condensation. The rate of gas diffusion through the membrane is linearly proportional to the partial pressure of the oxygen on both sides of the membrane[2]. The rate of diffusion is also highly temperature dependant. The gas must first pass through this membrane, hence the membrane in conjunction with the electrolyte between the membrane and the cathode, controls the response

time of the sensor. The membrane is set at manufacture and the speed at which gases pass through it cannot vary unless the membrane ages or is affected by condensation or contamination.

Water on the surface of the membrane acts as a barrier, the oxygen will move through the water at a certain (slower) rate[3] then through the membrane into the sensor.

Since oxygen is reduced at the cathode, the partial pressure on the cathodic side of the membrane is lower, generating a driving force which is linearly dependent on the oxygen partial pressure, so the rate of gas diffusion (and hence sensor output) is linearly dependent on the oxygen partial pressure (ie. the output of the oxygen sensor is linear with a rising partial pressure of oxygen).

A simple example of this is:

An oxygen sensor reads 10mv in air at sea level (PPO_2 = 0.20945 bar). If the PPO_2 is raised to 1.0 bar then the sensor output rises to 47.74mv.

1.0/0.20945 = 4.774

4.774 x 10mv = 47.74mv

CONCEPT SUMMARY

Rebreather galvanic oxygen sensors exhibit the following characteristics:

- Sensor output varies linearly with oxygen concentration from 0 to 100%.
- Any change in atmospheric pressure linearly affects the oxygen partial pressure and the sensors are linearly dependent on ambient pressure as well.
- Since the gas must diffuse through a solid polymer membrane, the rate of diffusion is dependent not only on the gas partial pressure but also on the diffusivity of the membrane (which is affected by condensation etc.).

The diffusivity of a polymer membrane is highly temperature dependent, typically 2.5%/K. This is corrected by using a Negative Temperature Coefficient (NTC) thermistor sensor inside the body of the oxygen sensor to compensate for temperature changes.

During thermal transients (rapid thermal changes) the membrane diffusivity and the NTC thermistor may not be in phase and significant PPO_2 reading errors can result.

Diffusion through a polymer membrane is relatively slow and, while they will respond rapidly (within 10 seconds) to approximately 90% of the oxygen partial pressure, the remaining 10% can take 20 to 60 minutes to fully register. The diffusion rate is (again) a function of condensate on the membrane.

Partial pressure sensors are linearly dependent on ambient pressure. In a Rebreather application the sensor must be 'balanced' i.e ambient pressure is allowed into both ends of the device. If one side were closed to ambient pressure, then the output would rise with both pressure (depth) and PPO_2 rather than just PPO_2 as in the balanced device.

In summary; partial pressure sensors respond linearly to changes in PPO_2, require temperature compensation, have a slow response time and, if designed correctly (balanced), show no transient behaviour when exposed to pressure changes. They are unaffected by most other gases except Chlorine and high levels of CO_2 (much higher than physiological levels experienced in rebreather systems).

In a known environment and within the device's operational limits, they are reasonably stable and reliable. They have a 'life span' (primarily as a function of the oxygen level they are exposed to). This life span requires that they are regularly calibrated and periodically replaced.

If they are operated outside of their design specification, they can become unreliable and inaccurate.

Figure 1 *- Oxygen sensor assembly*

Figure 2 *- Oxygen cell showing thermistor*

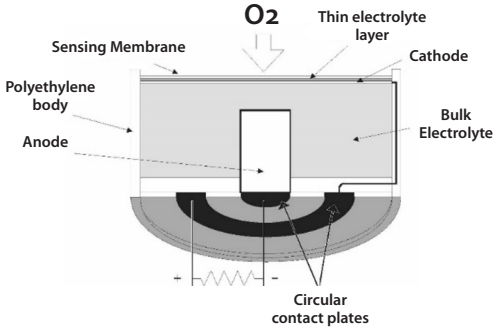

Figure 3 *- Oxygen sensor cross section*

FAILURE MODES

From the previous section, the primary[4] failure modes can be summarised as:

- Faulty or inaccurate temperature compensation – thermistor issues
- Reading a higher than actual PPO_2 – electrolyte depletion (heat stress/leak)
- Reading a lower than actual PPO_2 – anode depletion/current limiting (aging)
- Slow and inaccurate reading – membrane diffusion issue/damage

USING OXYGEN SENSORS IN A REBREATHER

As discussed, aside from age, temperature and humidity can have major effects on the performance of an oxygen sensor.

Both of these conditions occur in a rebreather to a greater extent.

Looking at temperature first, it is apparent that if the oxygen sensor is temperature compensated from 0 to 50°C then the position of those sensors within the rebreather should ensure that they are never exposed to more than 50°C throughout transport, calibration or a dive. Under CE EN14143 there is a PPO_2 sensor tracking test, which measures the accuracy of the sensors over a time period at a range of ventilation rates and depths and with different gases. If this test is passed, this confirms the suitability of a sensor/rebreather system for manned use. As a designer, without conducting this or similar tests, it will not be possible to assess if the sensors are being exposed to too great a temperature. Excessive temperatures can also damage the sensors by evaporating the electrolyte. This why this test, and ensuring storage temperatures are also not exceeded, is vital to maintain 'sensor health' and accuracy while in use.

If the bulk electrolyte evaporates, bubbles may be formed in the remainder and this will manifest as erratic readings.

If the electrolyte layer between the membrane and the cathode evaporates or leaks, it usually displays itself as a higher than normal output ie. the molecules of oxygen are transported to the cathode faster.

Humidity specifications for sensors vary. Some reference a maximum Relative Humidity (RH) of 50% and some 99%. Air leaving the mouth has an approximate temperature of 35°C and 95% RH. This means that the sensors in a rebreather are normally exposed to at least this RH.

Oxygen sensors operate accurately in a stable temperature and humidity environment. Due to rebreather design this may not be the case; the effect being that water vapour condenses and form droplets that affect the diffusion of gas across the sensor's membrane.

As temperature and pressure also affect RH, as these are changing all the time in a re-breather and because the sensors (when multiple sensors are used) will be in slightly different positions relative to gas flow, they will always exhibit slightly different readings. However, this variation is acceptable and can be dealt with within the control system electronics.

Calibration

A healthy and well-designed sensor will calibrate accurately in air (single point calibration) at the surface. It will then accurately read elevated PPO_2 correctly because it is linear in its response to changing PPO_2.

However, for as accurate calibration as possible, the calibration should take place once the absorbent canister has reached operating temperature (and humidity) and once the sensor has fully reacted to the change (up to 20 minutes). Without allowing for this, a PPO_2 content could be registered with a significant error. In operational terms, this would mean that either the gas in the breathing loop would be lower in oxygen than actually reported by the system, the body would absorb more nitrogen than the decompression algorithms had calculated, and the risk for DCS would be higher for the diver or the risk of oxygen toxicity is increased.

In addition, due to sensor aging and therefore current limiting, the sensor may calibrate correctly in air (or even 100% oxygen at the surface) but will not accurately measure elevated PPO_2's (above 1.0) at depth.

Electronically controlled rebreathers using galvanic sensors (and any PPO_2 display) have a method for converting a sensor's output (in air or 100% oxygen) during the calibration process to compensate for degradation of the sensors (reduction of output as a function of age). This process, if conducted incorrectly, can produce significant errors.

A final issue with calibration is that the calibration constants are not stored in the device; they are a function of the interface electronics. Therefore, if a sensor in a rebreather is swapped into another position, its calibration will now be inaccurate and the rebreather will not control/report PPO_2 correctly.

THE FUTURE – DIGITAL SENSORS

Digital Oxygen Sensor Principles

Digital oxygen sensors use an optical oxygen sensing element for gas measurements based on unique luminescent dyes, which are excited with red light and show an oxygen-dependent luminescence in the range of near infrared light (NIR).

The red-light excited sensor dye shows luminescence, which decreases with increasing oxygen levels (quenching effect). High NIR emission occurs at low oxygen levels and low NIR emission at high oxygen levels.

The measuring principle is based on sinusoidally modulated red excitation light. This results in a phase-shifted sinusoidally modulated emission in the near infra-red spectrum as a function of the number of oxygen molecules present. The sensor measures this phase shift, which is then temperature compensated, linearized, and converted into units of oxygen partial pressure based on the so called "Stern-Vollmer-Theory".

The principle is very robust. It shows virtually no interferences to other gases, has a very low drift, and the sensor is fully solid-state. It is an absolute sensor that accounts for atmospheric pressure, temperature and humidity and, as such, gives a 'true' reading of PPO_2 rather than one estimated based on a daily calibration procedure. Unlike galvanic oxygen sensors, it does not show significant output loss over time. The optics and electronics are hermetically sealed from the measured gas. The sensor has a factory calibration that then requires minimal adjustment (once or twice during the lifecycle) which can be conducted by a trained technician. The sensor features built in temperature compensation and a robust digital interface that provides oxygen partial pressure values for the control system. No additional signal conditioning is necessary.

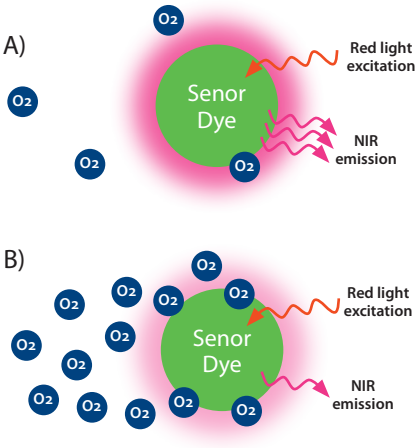

Figure 4 - Sensitivity to Oxygen Partial Pressure

The five key elements that make this design of sensor ideal for use in life support systems are:

- low power
- low cross sensitivity (reaction with other gases)
- reliability (based on a reduction of failure modes)
- response time/accuracy
- limited user interaction (recalibration) requirements.

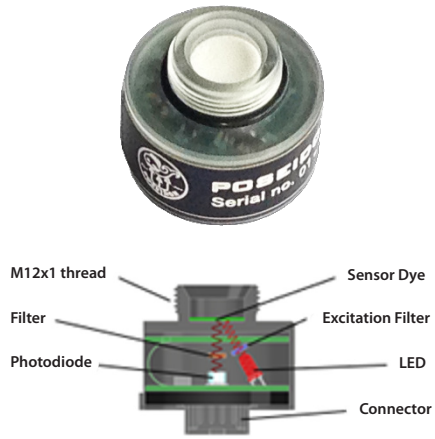

Figure 5 - Sensor Construction

FAILURE MODES

The basic sensing element is a light emitting diode and associated sensor. The failure mode of these is binary (on or off): The sensor generates an output signal, or it does not. This failure is easily compensated for/reported in software and corrective action is easily defined.

The interface is digital and again, using simple software processes, the data can be defined as 'good' or 'bad' and the relevant action taken. This also removes the issues related to analogue interfaces (amplifiers) associated with galvanic sensors (calibration errors etc.).

The sensor, with its on-board memory, and interface also allow for the implementation of 'black box' recording systems.

The encapsulated nature of the sensors makes them very robust.

FEATURES

- Reduced failure modes
- High accuracy
- Factory calibrated with no need for regular calibration
- Low drift
- Long life Minimum lifetime (>50,000.000 measurements)
- Fast response (t90<5s)
- Temperature compensation
- Low power consumption
- Electronics hermetically sealed from the sensing environment by a transparent window
- Lead free
- EMC tested - ESD protected interface
- Robust digital communication interface
- On-board memory for sensor ID and analysis functions

REBREATHER USE

With the features highlighted, digital oxygen sensors offer considerable safety advantages over their analogue counterparts and a through life cost reduction associated with mission readiness (MRT) and maintenance time.

They can be fully supported with a simple digital interface and embedded into most systems.

The largest improvement from a user perspective is the removal of the need to regularly recalibrate which can be a very time consuming and a potentially inaccurate process and safety issue. This, combined with other digital sensors (CO_2, gas supplies etc.) again make further reductions in mission readiness time and maintenance. A typical MRT for a fully digital system being under 10 minutes.

Figure 6 *- MCM100 Hub oxygen sensors*

[1] Faraday's law
[2] Fick's Law
[3] Henry's Law
[4] Failure modes can also develop in the electrical connection and electronic amplifier circuits of the rebreather