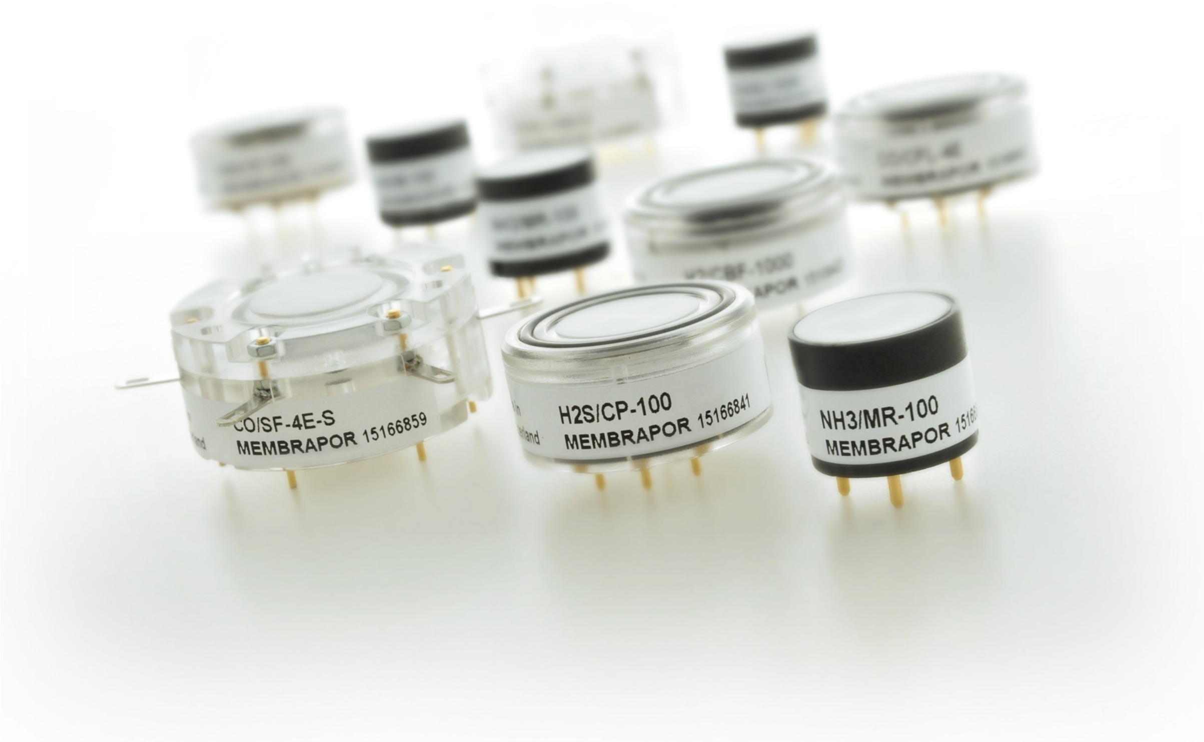
MEMBRAPOR

ELECTROCHEMICAL GAS SENSORS



Application Note MEM1

Electrochemical Gas Sensor

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MEM1 Application Note Electrochemical Gas Sensor

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1 General

MEMBRAPOR is producing gas sensors for OEMs of gas analyzers and detectors. It is expected that users of MEMBRAPOR products are professionals in the field of gas analysis and that they know their responsibility and their local regulations.

This application note is about **electrochemical** gas sensors for toxic gases and should serve as a guidance. This documentation is not claimed to be complete and MEMBRAPOR does not accept a liability for any consequential losses, injury or damage resulting from the use of this document or the information contained within it.

2 Usage of the Sensor

- Never solder connectors directly onto sensor pins. Connection should be made via a PCB mounting socket. To connect a sensor with wires, use the Slim- or Standard-size which have soldering tags.

  WARNING: SOLDERING TO PINS WILL RENDER YOUR WARRANTY VOID.

  Suitable sockets are proposed in chapter 7.

- Do not bend or twist soldering tags (Slim- and Standard-size). Order sensors without soldering tags if you do not need them.
- If there is a short-cutting spring, remove it before plugging the sensor in.
- Do not remove the white anti-condensation membrane.
- Sensors must not be exposed to temperatures, humidities and pressures outside the specified range in the respective data sheets.
  General: The sensors are not suitable for temperatures over 50 °C and for the use in vacuum chambers.
- Sensors should not be exposed to organic vapor as it may influence the baseline or even cause physical damage to the sensor body (see chapter 18.1).
- At the end of product's life, sensors can be returned to MEMBRAPOR for professional and environment-friendly disposal.

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3 Intrinsic Safety Considerations

An electrochemical sensor is a cell which produces small currents and voltages, and is not able to store large quantities of energy.

The current of the sensor increases linearly over the recommended operating range of the gas concentration and is measured as the sensor output:

sensor sensitivity [nA/ppm] x gas concentration [ppm] = output signal [nA]

3.1 Current and Open Circuit Voltages for Toxic Gas Sensors

Maximum current in normal operation: < 0.2 mA

Maximum short circuit current: < 0.5 A

Maximum voltage in normal operation: < 1.5 V

Maximum open circuit voltage: < 1.5 V

Note:

IEC 60079 – 11, 5.6 Simple apparatus:

“The following apparatus shall be considered to be simple apparatus: Sources of generated energy, which do not generate more than 1.5 V, 100 mA and 25 mW.”

4 Product Safety

A MEMBRAPOR gas sensor is not considered hazardous. Should the housing be damaged, the electrolyte inside the sensor may leak out. Exposure to the sensor electrolyte, which is diluted sulfuric acid, is the only risk that may potentially prove hazardous to health. In the event of skin contact, rinse with plenty of water and seek medical advice.

The MSDS document can be downloaded at www.membrapor.ch

5 Storage and Transport

Sensors should be stored in their original packaging below 30 °C and between 30 % and 90 % RH. Do not store sensors together with organic solvents or flammable liquids.

Electrochemical gas sensors are classed as non-dangerous and may be transported without special packaging or labeling. Nevertheless, you are advised to check any local regulations.

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6 Sensor Housing

MEMBRAPOR gas sensors are available in different housings, made of polycarbonate. The housing determines the size of the electrodes. Miniature-size sensors contain smaller electrodes than the other housings and thus provide smaller signal outputs.

Compact-, Slim- and Standard-size sensors have an air vent on the back, which in some applications is important. Due to their large electrodes they are more resistant to poisoning of the catalyst.

If the connection is made by soldering, then Slim- or Standard-size sensors are the appropriate choices as they have soldering tags for this purpose. Never solder connectors directly onto sensor pins, this will render your warranty void. Do not bend or twist soldering tags.

7 Connecting the Sensor

A sensor has 2 - 4 pins at the bottom for the electrical and mechanical contact. The PCB should have sockets where the sensor with its pins can be plugged-in. In the table below suitable sockets are listed from various suppliers.

Sockets with a clip give generally a safer electrical connection with the pin. They should be considered in case of vibrations or frequent plugging.

The diameter of the pins is 1.0 mm (0.04 in) in the case of Compact-, Slim- and Standard-size sensors, and 1.5 mm (0.06 in) in the case of Miniature-size sensors.

Company	**Part number / Feature**	**Suitable for**
Mill-Max www.mill-max.com	0322-0-15-15-34-27-10-0	Compact, Slim, Standard
	9801-0-15-15-23-27-10-0	Miniature
Andon Electronics Corporation www.andonelect.com	9876-2-R15 / with clip	Compact, Slim, Standard
	9879-1-R15 / with clip	Miniature
MultiContact www.multi-contact.ch	BS1 41.0053 / with clip	Slim, Standard
Bürklin www.buerklin.com	20F2611 (0–5050865–5)	Compact, Slim, Standard
	20F2617 (2–5050871–3)	Miniature

Table 1 Suitable sockets to connect sensors

The Slim- and Standard-size sensors have additionally soldering tags, which can be used for the electrical contact. Do not bend or twist the tags. Order sensors without soldering tags if you do not need them.

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8 Label

The label on MEMBRAPOR gas sensors includes the sensor type, the serial number and a 2D-Code which contains both information.

8.1 Sensor Type

Every sensor type is described with a logical product code:

[Gas] / [Size Sensor] [*Option* Filter] [*Option* Variation] - [Measurement Range] - [*Option* 2 *or* 4 Electrodes] - [*Option* Slim *if S-size*]

Examples:

CH2O/C-10	For Formaldehyde, Compact-size, for 0-10 ppm
NO/SF-2000-S	For Nitric Oxide, Slim-size, with filter, for 0-2000 ppm
NH3/MR-100	For Ammonia, with fast response, for 0-100 ppm

8.2 Serial Number and Date of Manufacture

With the individual serial number, MEMBRAPOR can trace all test results and production data, including the whole supply chain.

The date of production is encoded in the first 4 digits: yyCW.

yy: The year (Last 2 digits, e.g. 14 means the year 2014)

CW: The calendar week in that year.

8.3 2D-Code

On the white label is a two-dimensional matrix bar code printed. It is encoded in "DataMatrix Code", ECC type: 200. It includes the serial number and the sensor type. These two information are separated with a space.

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9 Sensor Principle

9.1 Electrochemical Gas Sensors in General

Electrochemical sensors operate by reacting with the analyte and producing an electrical signal. Most electrochemical gas sensors are amperometric sensors, generating a current that is linearly proportional to the gas concentration. The principle behind amperometric sensors is the measurement of the current-potential relationship in an electrochemical cell where equilibrium is not established. The current is quantitatively related to the rate of the electrolytic process at the sensing electrode (also known as working electrode) whose potential commonly is kept constant using another electrode (the so-called reference electrode).

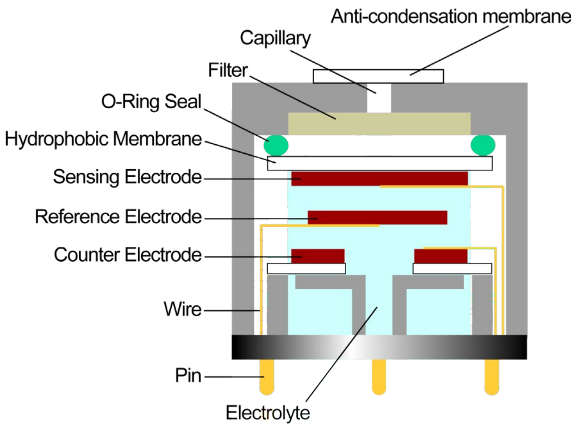

Figure 1 Working principle of an electrochemical gas sensor

9.2 Working Principle

A MEMBRAPOR electrochemical gas sensor works as follows: Target gas molecules that come in contact with the sensor first pass an anti-condensation membrane which serves also as a protection against dust. Then the gas molecules diffuse through a capillary, potentially through a subsequent filter, and then through a hydrophobic membrane to reach the surface of the sensing electrode. There the molecules are immediately oxidized or reduced, consequently producing or consuming electrons, and thus generating an electric current.

It is important to note that with this approach the amount of gas molecules entering the sensor is limited by the diffusion through the capillaries. By optimizing the pathway, in accordance with the desired measurement range, an adequate electrical signal is obtained.

The design of the sensing electrode is crucial in order to both achieve a high reactivity towards the target gas and to inhibit undesired responses to interfering gases. It involves a system of three phases: solid, liquid and gaseous, and all are involved in the chemical recognition of the analyte gas. MEMBRAPOR is passionately dedicated to tailor this system and obtain high-performance gas sensors.

The electrochemical cell is completed by the so-called counter electrode which balances the reaction at the sensing electrode. The ionic current between the counter and sensing electrode is transported by the electrolyte inside the sensor body, whereas the current path is provided through wires terminated with pin connectors.

Commonly, a third electrode is included in an electrochemical sensor (3-electrode sensor). The so-called reference electrode serves to maintain the potential of the sensing electrode at a fixed value. For this purpose and generally for the operation of an electrochemical sensor a potentiostatic circuit is needed.

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9.3 Sensor Signal

The output signal of a MEMBRAPOR gas sensor corresponds to the concentration of a gas rather than to its partial pressure. Hence, it is possible to use a MEMBRAPOR sensor at different altitudes or even underground, independent at which atmospheric pressure the device was calibrated.

A deeper and scientific explanation of the sensor output and the pressure dependence can be found in the document MEM4.

10 3-Electrode Sensors – Design of Potentiostatic Circuit

To operate an electrochemical sensor a control circuitry is required, referred to as the potentiostatic circuit. For a 3-electrode sensor the main purpose is to maintain a voltage between the reference electrode (Ref) and the sensing electrode (Sens, also known as working electrode) to control the electrochemical reaction and to deliver an output signal proportional to the current produced by the sensor.

The Sens responds to the target gas, either oxidizing or reducing the gas, creating a current flow that is proportional to the gas concentration. This current must be supplied to the sensor through the counter electrode (Cnt).

At the Cnt the opposite redox reaction takes place, completing the circuit with the Sens. The potential of the Cnt is allowed to float. When gas is detected, the cell current rises and the Cnt polarizes with respect to the Ref. The potential of the Cnt is not important, as long as the circuit can provide sufficient voltage and current to maintain the correct potential of the Sens.

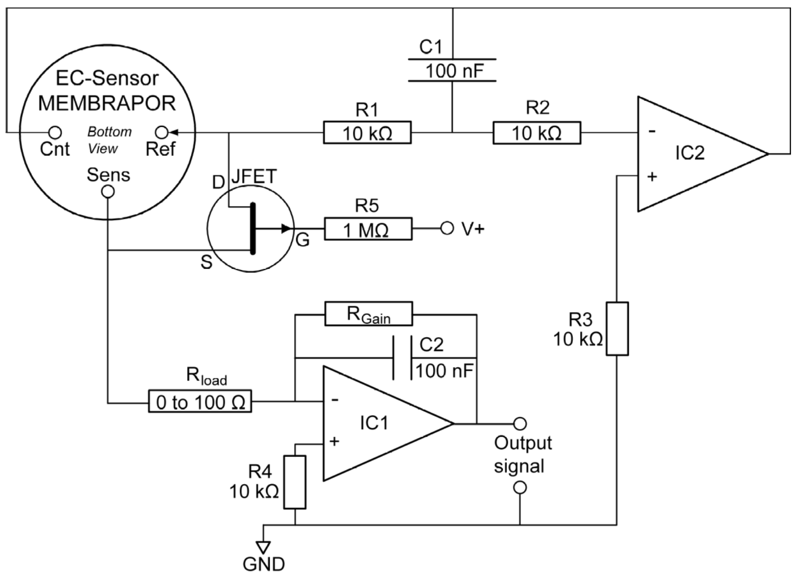

Figure 2 Schematic diagram of the electronic circuit for 3-Electrode-sensor

The measuring circuit for the electrochemical sensor is a single stage op amp IC1 in a transimpedance configuration. The sensor current is reflected across R_{GAIN}, generating an output voltage relative to the virtual earth GND. C2 reduces high frequency noise. The load resistor R_{load} is a compromise between fastest response time and best signal-to-noise ratio. The recommended value is given in the sensor data sheet.

The control op amp IC2 provides the current to the Cnt to balance the current required by the Sens. The inverting input into IC2 is connected to the Ref and must not draw any significant current from it.

The JFET is shorting the Ref to the circuit common when the circuit power is switched off.

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This ensures that the Sens is maintained at the same potential as the Ref. This state for unbiased sensors ensures that the sensor is ready immediately when switched on.

Sensors which need a bias voltage have not to be shorted. In opposite, it is recommended to hold the voltage (mostly 300 mV) all the time. This can be realized with a button cell during power off.

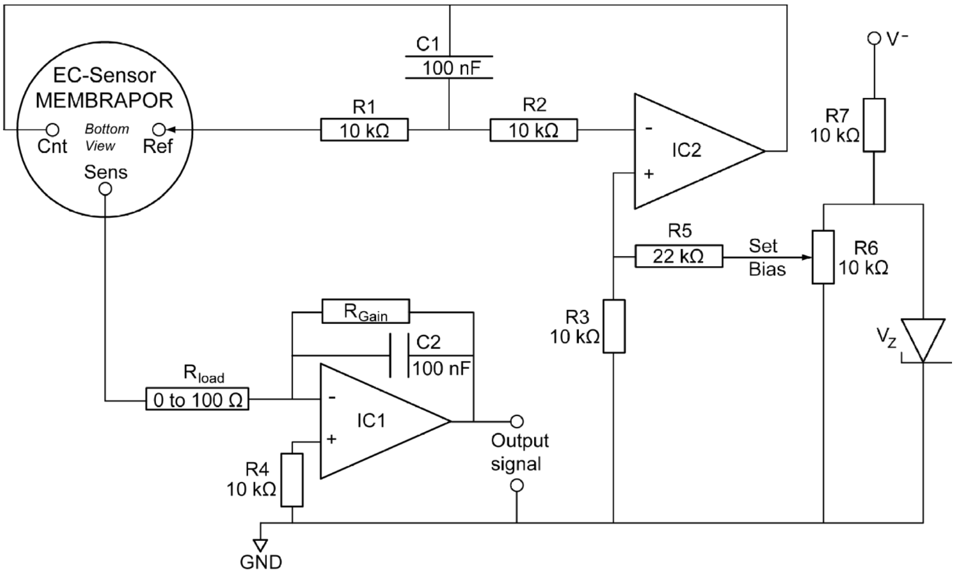

Figure 3 Schematic diagram of the electronic circuit for biased 3-Electrode-sensor

11 2-Electrode Sensors

A 2-Electrode sensor has the disadvantage that the potential of the sensing electrode can shift away. This occurs mainly when it is exposed to the target gas. Therefore it is not recommended to use a 2-electrode sensor for continuous measurement. Other disadvantages are stronger temperature dependence and lower signal output, compared to 3 or 4-electrode sensors.

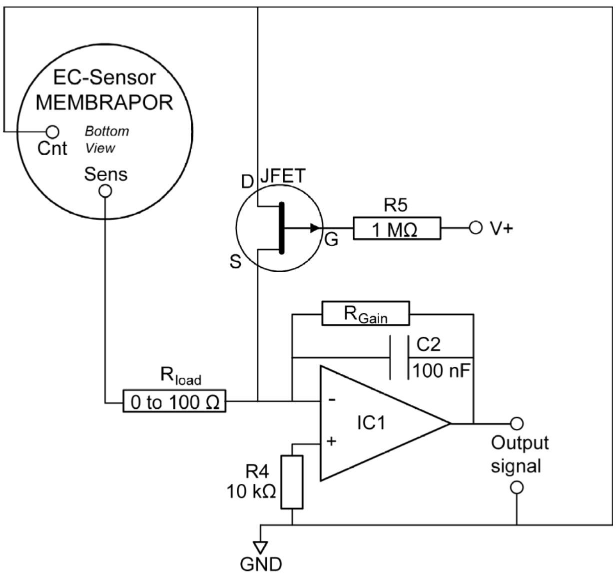

Figure 4 Schematic diagram of the electronic circuit for 2-Electrode-sensor

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12 4-Electrode Sensors

4-electrode sensors are the most sophisticated electrochemical sensors. They have an additional electrode, the so-called auxiliary electrode (Aux), that gives additional information about the state of the sensor. MEMBRAPOR produces 2 different kinds of 4-electrode sensors:

- Hydrogen-compensated sensors
- L-type sensors for low concentrations

These are completely different types of sensors, where the Aux adopts different functions. However, the basic potentiostatic circuit is the same:

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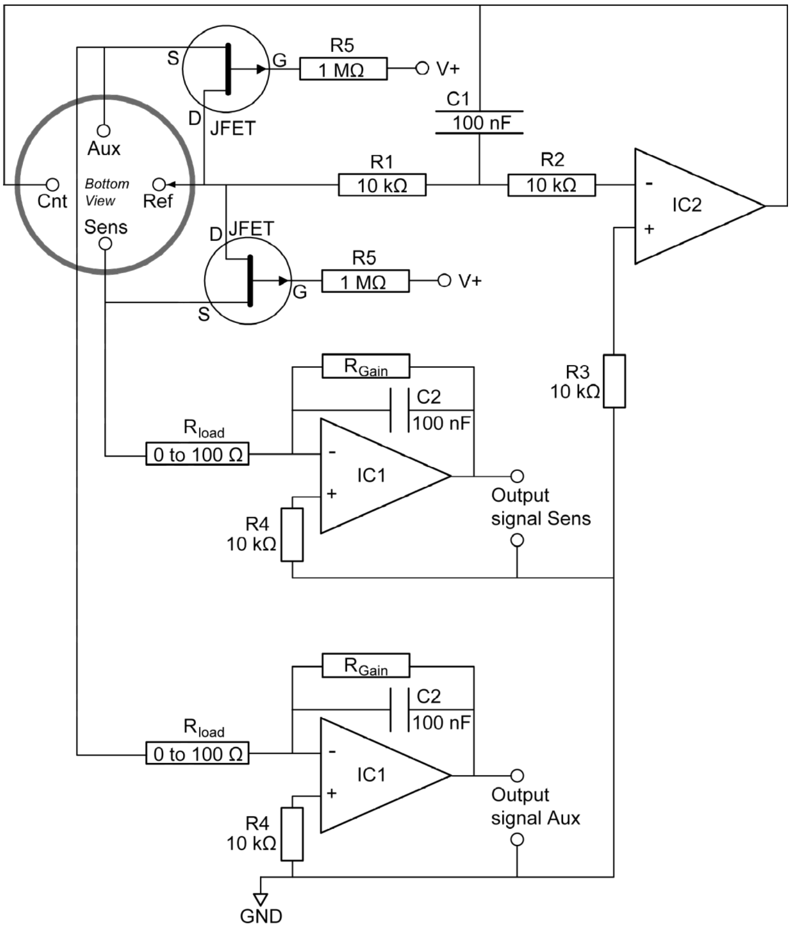

Figure 5 Schematic diagram of the electronic circuit for 4-Electrode-sensor

12.1 Hydrogen-Compensated Sensors

This type of MEMBRAPOR 4-electrode sensor allows to compensate for an interfering gas which is not possible to discriminate with filters or other techniques. The CO/SF-4E-S is a very popular gas sensor in flue gas/stack gas monitoring and an example of a hydrogen-compensated carbon monoxide (CO) sensor. While both the oxidation of CO and interfering hydrogen (H_2) occur at the sensing electrode, the signal at the auxiliary electrode is almost exclusively due to H_2. With two signals caused by two gases the concentrations can easily be calculated and thus, a highly accurate CO concentration is obtained in applications where 3-electrode sensors would fail.

12.2 L-Type Sensors for Low Concentrations

This type of MEMBRAPOR sensor allows to decrease the detection limit and increase the resolution compared to 3-electrode sensors. The signal of the auxiliary electrode is used to correct for the following effects:

- Drift of the baseline caused by changes in temperature
- Drift of the baseline caused by interference

Not corrected are cross-sensitivities due to interfering gases.

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13 Gas Sampling System

13.1 Positioning of the Sensor

The orientation of a MEMBRAPOR sensor has no influence on its operation.

In a device which is equipped with a pump, preferably the sensor is installed upstream of the pump. This minimizes any loss of analyte gas and any effects resulting from shock pressures caused by membrane pumps.

13.2 Flow Rate

When using a pump or mass flow controllers, the flow rate of the gas sample must be high enough to avoid depletion of the analyte. If a dependence of the flow rate is observed then the flow must be increased or the cross-sectional area above the sensor must be reduced. It is generally recommended to have a low dead volume above the sensor top. Typical cases, where depletion occurs, are while measuring NO_2 gas and in general with high sensitive sensors and low gas concentrations.

13.3 Discontinuous measurement

Some gases, like hydrogen sulfide (H_2S) or ammonia (NH_3), can affect the sensing capability of a sensor. Additionally, in some applications like biogas, there are additionally further sulfur containing compounds which can irreversibly poison the sensor. See chapter 18.2.

In such a situation the solution is to measure in discontinuous mode. In this manner the operation time will last more years. Conversely, the lifetime can be shortened to a few or even one month when measuring continuously.

A typical cycle in such a discontinuous mode is as follows:

- 3 min measurement
- 10 till 30 min purging with fresh air

Usually, the fresh air is obtained by tubing from the outside.

13.4 Oxygen

All gas sensors for reducing gases (CO, H_2, H_2S, NO...) require oxygen (O_2) to provide the counter-reaction at the counter electrode.

But there are several possibilities to measure in a gas sample without O_2:

- Short time measurement of a few minutes. Before and after the measurement, the sensor is exposed to ambient air. In this way, it has enough O_2 dissolved in the electrolyte.
- Compact-, Slim- and Standard-size sensors have a little hole on the back side for O_2 access. These types can be front-mounted to a pipe with the gas stream and get O_2 from ambient air from the back side.
- Discontinuous measurements. Gas sampling system with valves which switch between gas sample and ambient air periodically.

The same measures can be applied to gas samples with humidities outside of the specified range.

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13.5 Humidity

General

Most electrochemical gas sensors contain a liquid, aqueous electrolyte which is in equilibrium with the humidity content of surrounding air. At dry conditions the electrolyte will lose water and gain water at high humidities. Most MEMBRAPOR sensors are specified to operate in the humidity range of 15 % to 90 % RH. However, for a short time the sensor can be operated outside the humidity range.

Sensor Performance

The sensitivity of a MEMBRAPOR gas sensor is **independent of the humidity** over the specified range. An abrupt change in humidity can cause a short term transient signal for some types of sensors. This effect is noted in the respective data sheets. Calibration with dry gas, when switching from ambient air, is such a situation. Thereby the first seconds of the sensor response are a superposition of this transient signal and the signal response to the change in gas concentration.

Ambient Air Monitoring

In ambient air monitoring the humidity can reach extreme values. This is not a problem as long it lasts only for a few days. The absorption and desorption of gaseous water by the sensor electrolyte is a slow process. It takes 10 - 30 days till the equilibrium is established.

Industrial Gas Monitoring

Continuous gas monitoring is possible in conditions where the relative humidity most of the time is between 15 % and 90 %. Expressed as dew points, these limits are -7 °C and 18 °C, if the operating temperature is 20 °C. Operating temperature means the temperature of the gas sample, which should be equal to the temperature of the sensor. In the graph below the limits of the dew point are depicted over the whole temperature range.

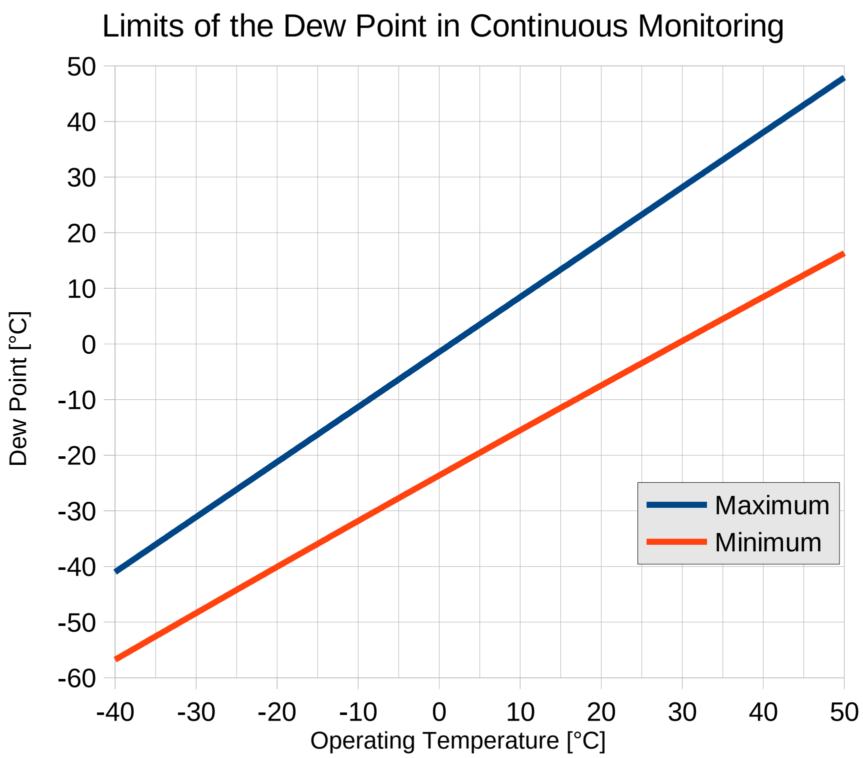

Figure 6 Allowed humidity range expressed as limits of the dew point of the gas sample

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Monitoring under complete dry or humid conditions can be realized with an ambient air purge cycle.

Extreme Conditions of Humidity

If a sensor is exposed for a very long time to a relative humidity over 90 %, then it will have absorbed so much water, that the inner electrolyte will leak. In such a case the sensor was used outside of warranted performance and is destroyed.

If a sensor is exposed for a long time to a relative humidity below 15 %, then it will dry out and give no signal. Most sensors can recover when they are stored at ambient air for a month. But it is possible that the sensitivity will be lowered and/or the response time increased.

Operation for extended periods outside the range of 15 % - 90 % relative humidity will invalidate the warranty.

The two extreme situations, leakage and drying-out, can be supervised. See chapter 16 for details.

13.6 Temperature

The temperature range, where a sensor can be used, is specified in the data sheet. Generally, the maximum temperature is +50 °C. Above this limit the sealing in the sensor housing might be affected and the electrolyte could leak out. Additionally, inner electrical contacts might be corrupted, which would result in a slow response and signal loss.

Low temperatures are harmless. But for some gases the signals at -40 °C can be very low.

In the case of temperature gradients in a gas sampling system, attention has be paid to avoid condensation onto the sensor head. A formation of droplets on the anti-condensation membrane will affect the gas entry and therefore the sensor response.

13.7 Pressure

Generally, electrochemical gas sensors are meant to be operated at atmospheric pressure ±10 %. However, MEMBRAPOR gas sensors can be used in a broader pressure range. Ask the MEMBRAPOR technical support team for help.

13.8 Partial Pressure versus Concentration

The signal of MEMBRAPOR gas sensors and therefore the calibration is not affected by changes in total pressure, or only to a small degree. In opposite to other gas sensors, MEMBRAPOR sensors give a signal proportional to the concentration of the analyte gas and not to its partial pressure.

The scientific explanation can be obtained from MEMBRAPOR's technical support team.

In practice, an instrument with a MEMBRAPOR gas sensor can be used at any elevation or underground, without the need to recalibrate it.

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14 Calibration

The performance of a sensor or the whole instrument, respectively, must be checked regularly with calibration gas. Exchange the sensor when its sensitivity is below 50 % of its initial value or if the response time is too high.

Calibrate the device with the gas sensor at conditions most similar to the intended usage. Use a gas mixture representing the gas matrix in the application. Perform the span-calibration with the target gas. In some rare cases the cross-sensitivity to a different gas can be used.

It is no problem at all to use calibration gas balanced solely in nitrogen, i.e. without oxygen. The sensor has enough oxygen inside for a time interval of calibration.

It is uncritical to use completely dry calibration gas mixtures. Within the time of calibration the sensor will not dry out.

MEMBRAPOR gas sensors without a bias voltage are ready for calibration/measurement within 3 minutes after power on. Sensors requiring a bias voltage need between 24 to 72 hours for stabilization of the baseline and adaption to the environmental temperature. Start a calibration/measurement when the baseline is stable.

The calibration interval depends on number of factors including application, environmental conditions, regulations and accuracy requirements. The long term output drift of a sensor gets smaller with time at constant conditions.

15 Temperature Compensation

The output signal (sensitivity) and the baseline of a sensor are temperature-dependent parameters. Generally, the sensitivity increases with increasing temperature and is at -40 °C much lower than at room temperature. Basically, this is given by the nature of the gas and its chemical reaction inside the sensor.

For some gases the baseline differs from zero, mostly at high temperatures and this especially with biased sensors.

It is highly recommended to acquire the temperature dependence curves with the whole instrument. The sampling system, the electronics, the interaction between the electronics and the sensor, all have a significant impact on the temperature dependence of the final measurement reading.

16 How to Check Sensor Functionality

The signal noise gives valuable information about the plugged-in sensor. Three cases can be distinguished: The signal noise

a) is too low, determined mainly by the circuit:
The sensor is drying out or poisoned

b) is as low as if no sensor would be plugged in:
The sensor has dried out completely or an electrical contact is lost

c) is too high:
Leakage of the sensor electrolyte is occurring

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17 Gases and Lifetime

The lifetime of a sensor depends heavily on the application. Mainly the exposition to certain gases and their concentrations have strong impacts. The lifetimes noted in this chapter are conservative values. It is absolutely possible that a MEMBRAPOR sensor reaches a lifetime of 5 years or even more.

17.1 C_2H_4, CS_2, H_2S, H_2O_2, HCl, HCN, NH_3, PH_3, SiH_4

A lifetime of >2 year can be expected for leak detection, discontinuous measurement (see chapter 13.3) or spot measurement. Continuous exposure, even at low concentrations, has to be avoided.

17.2 Acid, Alc, CH_2O, Cl_2, ClO_2, CS_2, NO_2, O_3, SO_2

A lifetime of > 2 year can be expected in the case of continuous exposure at low concentrations or spot measurements over the whole measurement range.

17.3 ETO, H_2

A lifetime of >2 years can be expected even in the case of continuous exposure.

17.4 CO, NO, O_2

A lifetime of >3 years can be expected even in the case of continuous exposure.

17.5 End of Life

The performance of a sensor should be verified with regular tests or calibrations. If a sensor has lost more than half of its initial output signal, it is recommended to replace it. In continuous monitoring the noise of the signal can be used to check the sensor functionality (see chapter 16 How to Check Sensor Functionality).

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18 Observable Effects of Certain Gases

18.1 VOCs

Volatile organic compounds (VOCs) should be avoided in applications where electrochemical sensors are used because they either dissolve in the electrolyte or adsorb onto the sensor's housing. Both effects can result in shifts in the baseline and/or changes in the overall sensor performance (sensitivity, response time...). Conveniently, the sensor is able to recover under clean air after a few days.

18.2 Sulfur Containing Compounds

Compounds containing sulfur strongly adsorb onto the catalytic surface, temporarily inhibiting the sensing reaction. Moreover, many of these compounds decompose and form a solid barrier. With prolonged exposure such processes lead to an irreversible decrease in sensitivity. This effect is known as poisoning of a catalyst.

Use sensors with filters (Option "F") if such gases are present in the intended application.

18.3 Silicones

Silicon compounds are known catalyst poisons.

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19 Selectivity and Cross-Sensitivity

MEMBRAPOR gas sensors belong to the most selective sensors. Still, some limitations are given due to the chemical nature of the reactions involved. **All cross sensitivity data contained in the data sheets refer to normal measurement conditions (20 – 25°C, 30 – 50 % RH, 900 – 1100 mbar pressure).**

19.1 SO_2 and NO_2

All sensors for sulfur dioxide (SO_2) show a significant cross-sensitivity to nitrogen dioxide (NO_2). NO_2 produces a signal in opposite direction to the SO_2 signal, as it is reduced and not oxidized as SO_2. There is no suitable filter material that at once blocks NO_2 and lets pass SO_2. Therefore, measuring SO_2 in applications where also NO_2 is present, e.g. in flue gases, one has to account for such negative signals when designing the electronic circuitry for a SO_2 sensor. Additionally, a sensor for NO_2 is needed to calculate the correct SO_2 concentration from the superimposed signals.

NO_2 sensors do not show a significant cross-sensitivity to SO_2 at normal concentrations. But to measure NO_2 near the detection limit with high SO_2 background, the same correction has to be done as described above.

19.2 NO and NO_2

In an electrochemical sensor nitrogen monoxide (NO) is oxidized to nitrogen dioxide (NO_2) and NO_2 is reduced to NO. These reactions have to be taken in account when both sensors are mounted in the same line of the gas sampling system.

19.3 CO and H_2

All sensors for carbon monoxide (CO) have a cross-sensitivity to hydrogen (H_2). With the A-type CO sensors from MEMBRAPOR it is strongly reduced and might be sufficient for many applications. Full discrimination is achieved with hydrogen-compensated 4-electrode sensors that give two signals and allow the exact calculation of both the CO and H_2 concentrations.

19.4 Filter options

Due to the target gases' chemical nature the application of filters is not always possible. Table 2 gives a short overview for which target gases, sensors with optional inboard filters are available and the main effect of the filter. More detailed information can always be found in the corresponding data sheet.

Gas	**Effect of filter**
CO	*Removes acidic gases*
CS2	*Removes acidic gases*
NO	*Removes effect of SO2*
NO2	*Removes O3*
SO2	*Removes H2S and HCl*

Table 2 Gas sensors with optional filter

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19.5 Filter Capacity

In applications like flue gas/stack gas monitoring the filter can be used up with time. Usually this happens within years. Check the relative sensor data sheets for the filter capacity values.

The transparent housings of MEMBRAPOR Compact-, Slim- and Standard-sized gas sensors have the advantage that one can verify optically if the filter of a CO sensor is used up. The change of purple to brown is visible by eyes and indicates that the filter capacity has reached its end.

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