# European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

## COST Action TD1105

## 1ST TRAINING SCHOOL

## Universitat de Barcelona, Spain, 13 - 15 June 2013

**Action Start date: 01/07/2012 - Action End date: 30/06/2016**

**2012 - 2013 (*Ongoing Action*)**


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COST is supported by the EU Framework Programme

European Science Foundation

ESF provides the COST Office through a European Commission contract

# Electrochemical Sensors

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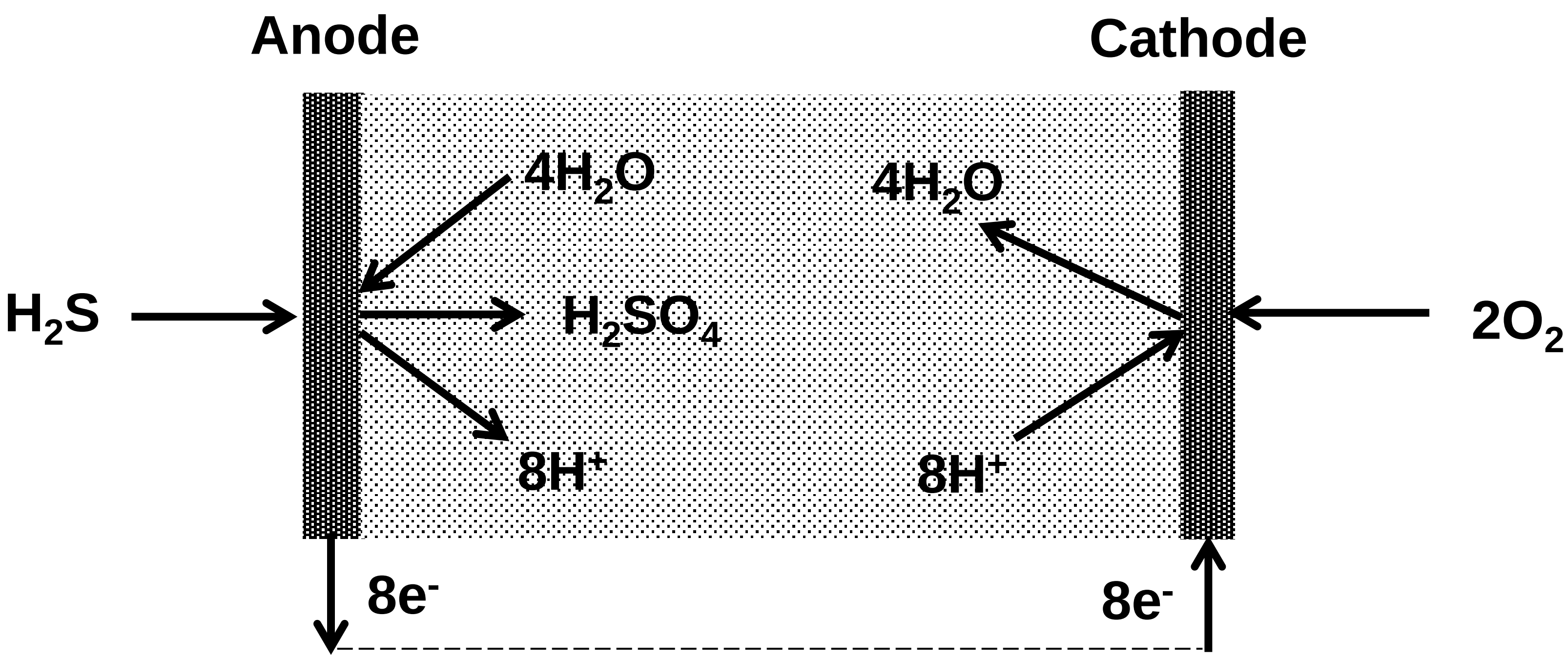


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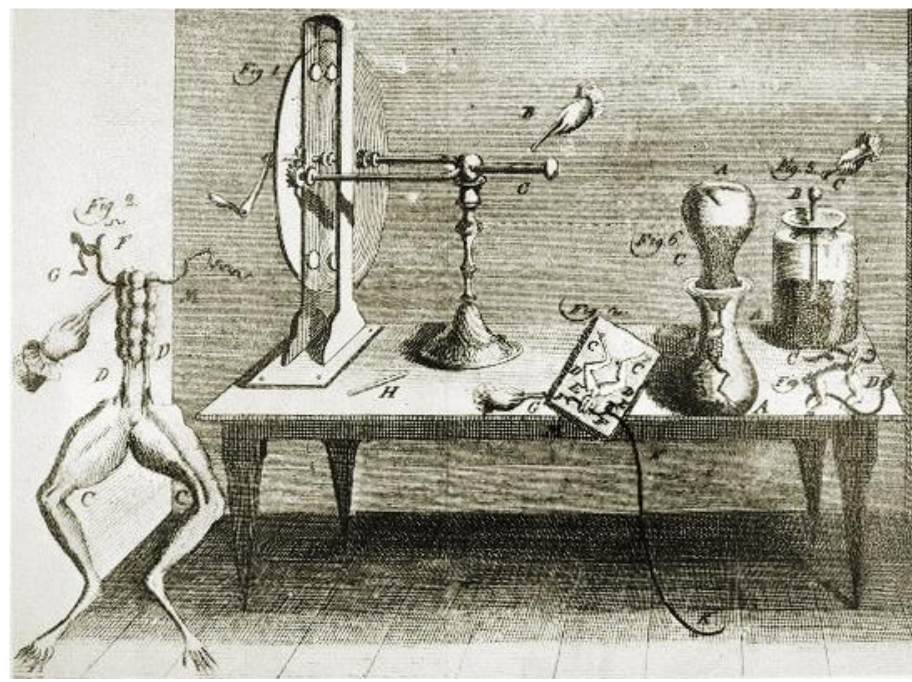
# Outline

# 0. Fundamentals

- Operation principle is relatively complex
- Easiest modelling: parallel batteries
- But: in the batteries all reaction components are included
- When the goal is a target gas (=missing reaction component) that has to enter the sensor, the electrochemical sensor provides a current
- Current is orders of magnitude lower than that of a battery
- If the reaction component is only available in limited amount and is, therefore, the limiting factor, then the current measured through a resistor is proportional to the concentration of the target gas

# Historical view: the beginning of the galvanic cell

- 1780: Luigi Galvani (ital. physician) discovers through experiments with frogs‘ legs the contraction of muscles when in contact with copper and iron
- For this, copper and iron need to be in contact
- Galvani built, substantially, an electrical circuit with 2 different metals, an electrolyte (sea water in the frog‘s legs) and a current “indicator“ (the muscle)
- --> Basis for the development of electrochemical cells (by Alessandro Volta)



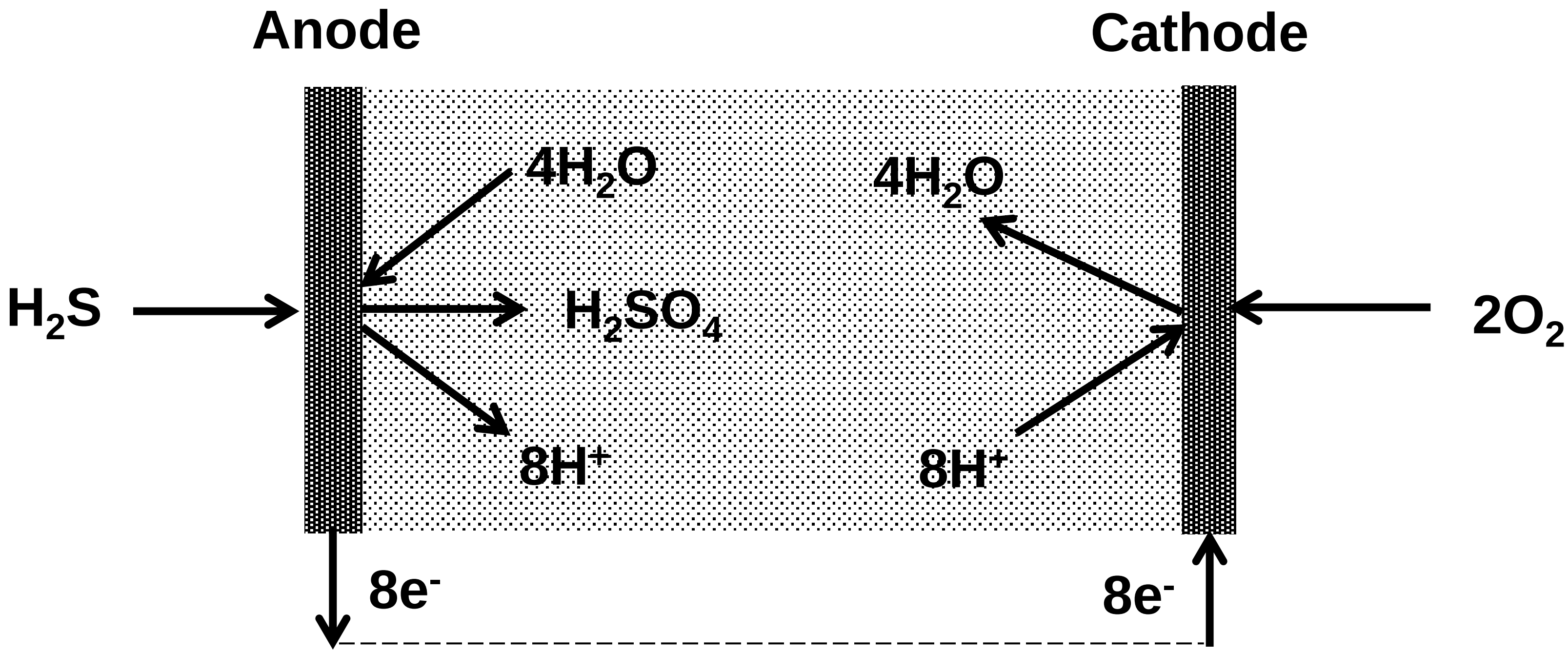
Source: Wikipedia

# 0. Fundamentals

- The basic principle relies on the exchange of electrons during the chemical reaction of 2 reaction components.
- Redox reactions
- Oxidation and reduction have to take place in separated areas
- The exchange of electrons occurs through an external electrical circuit, not through a reacting molecule
- Reactions take place at electrodes ("semi-cells") that are within the electrolyte

# 0. Fundamentals

## Example: oxidation of water-diluted sulphur hydroxide into sulphuric acid




The ions travelling from one to the other half-cells (from the anode to the cathode) are $H^+$ ions.

# 0. Fundamentals

**Example: oxidation of water-diluted sulphur hydroxide into sulphuric acid**

8 electrodes are liberated during the reaction, but are not seen in the overall reaction:

Overall reaction: $H_2S + 2O_2 \Rightarrow H_2SO_4$

Oxidaton of $H_2S$ (SC1) $H_2S + 4H_2O \Rightarrow H_2SO_4 + 8\,H^+ + 8e^-$

Reduction of $O_2$ (SC2) $2O_2 + 8\,H^+ + 8e^- \Rightarrow 4H_2O$



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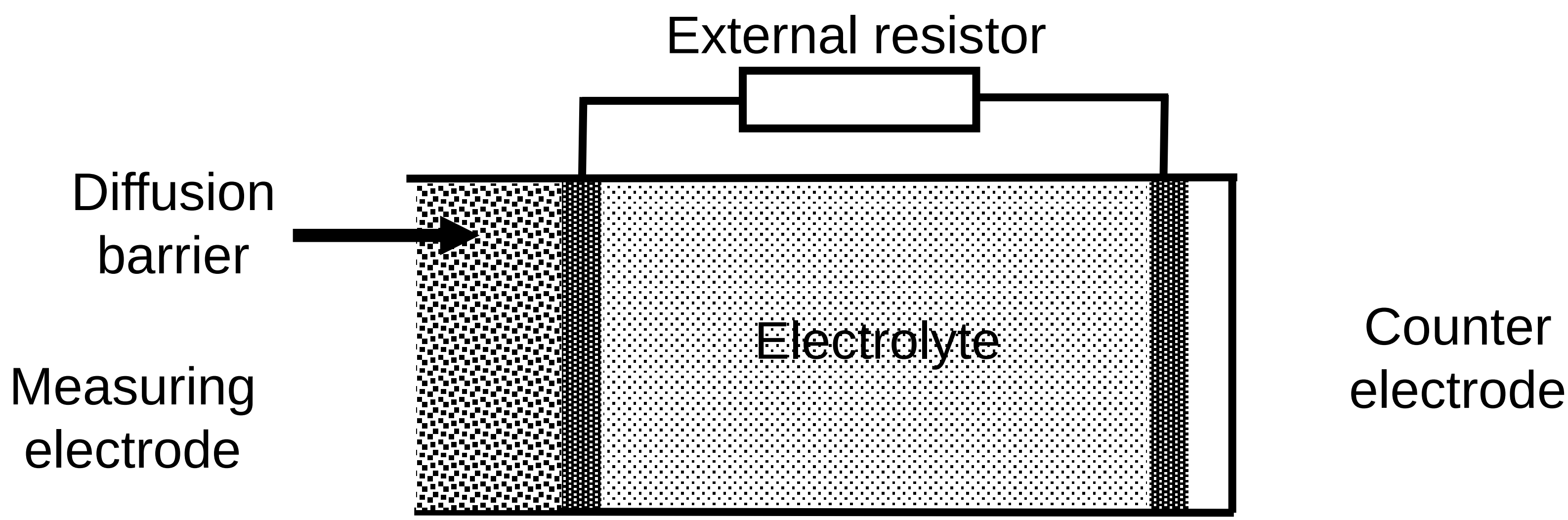
# 0. Fundamentals

- Electrochemical sensors are systems that provide an electrical signal proportional to the concentration of gas, because each electrochemical molecule that reacts releases at least one electron
- Electrohemical sensors operate, usually, according to the amperometric principle, i.e., the electrical signal is a current.
- The flow of electrons over the external circuit goes from the anode to the cathode
- Amperometry: measurement of the electrical current at constant voltage between the electrodes
- Voltametry: voltage changes with time
- The gas concentration is directly converted into an electrical signal. The conversion into another physical mangitude (heat, light, ...) is not required

# 1. Construction

## Schematical construction of an electrochemcial sensor

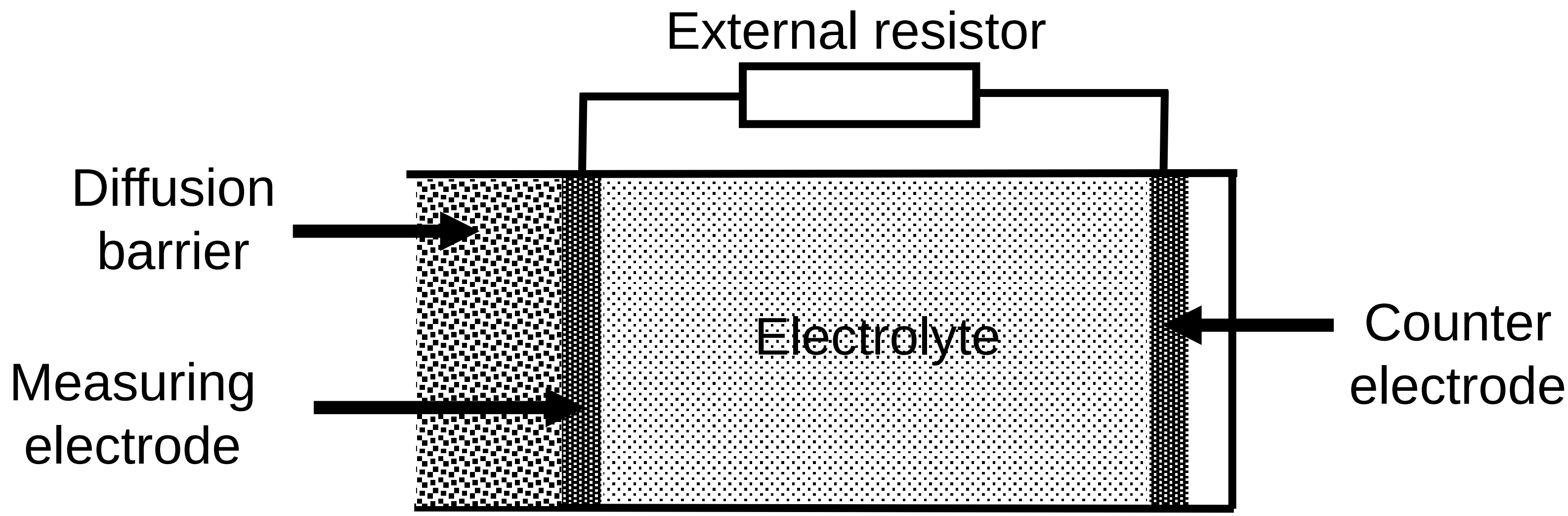



**Diffusion barrier:** Limits the gas mass‘ transport to the measuring electrode.

**Electrodes:** two similar gas-permeable electrodes. The counter electrode is in the inside of the sensor. The measuring electrode is such that it can come in contact with the atmosphere and the gas to be dectected. The electrodes have to be corrosion resistant and shouldn‘t react catalytically with other gases.

# 1. Construction

## Schematical construction of an electrochemcial sensor



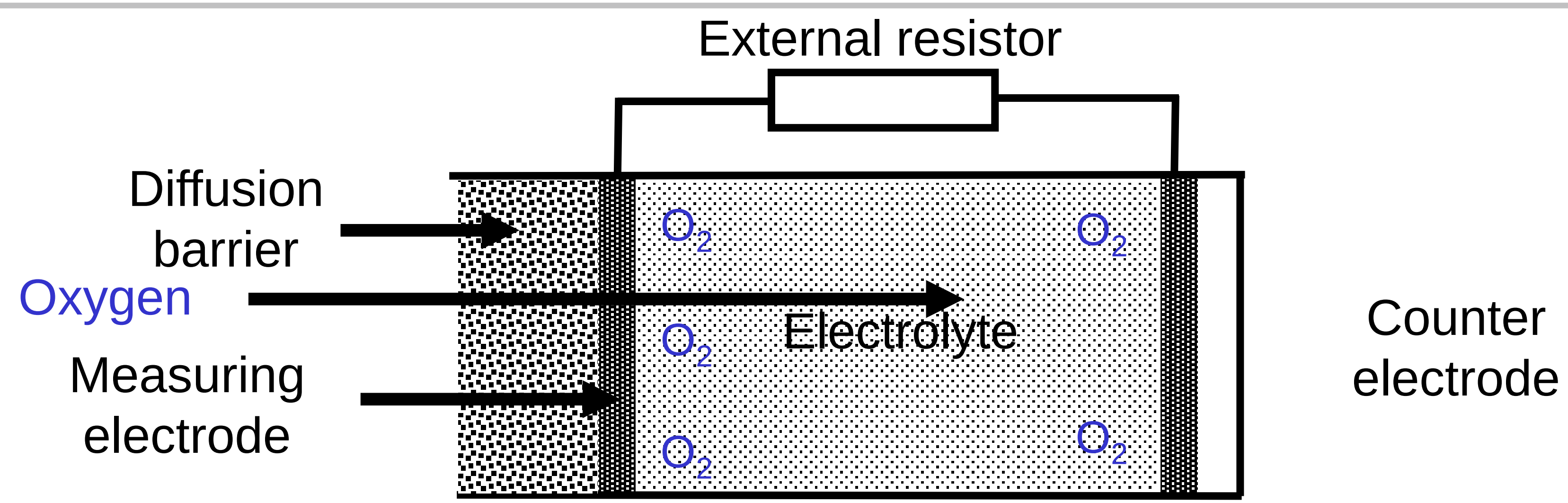

**Electrolyte:** concentrated aqueous ionic-conductive electrolyte between the electrodes:

Example: diluted sulphuric acid, neutral salts, basic NaOH or KOH.

**External circuit:** Low-resistive connection between the electrodes.

Measured magnitude: voltage drop at the external resistor

# 1. Construction




$O_2$ diffuses through the diffusion barrier -> Adsorption on both electrodes = air resting potential

$O_2$ , with the $H^+$ ions of the electrolyte, tends to form $H_2O$ in acid media

$$O_2 + 4\,H^+ + 4e^- \Rightarrow 2H_2O$$

Initially the Pt electrode provides the required electrons and, next, electrically loads its surface positively and generates an electrical field that prevents the further liberation fo electrons and, thus, no further transformation of the

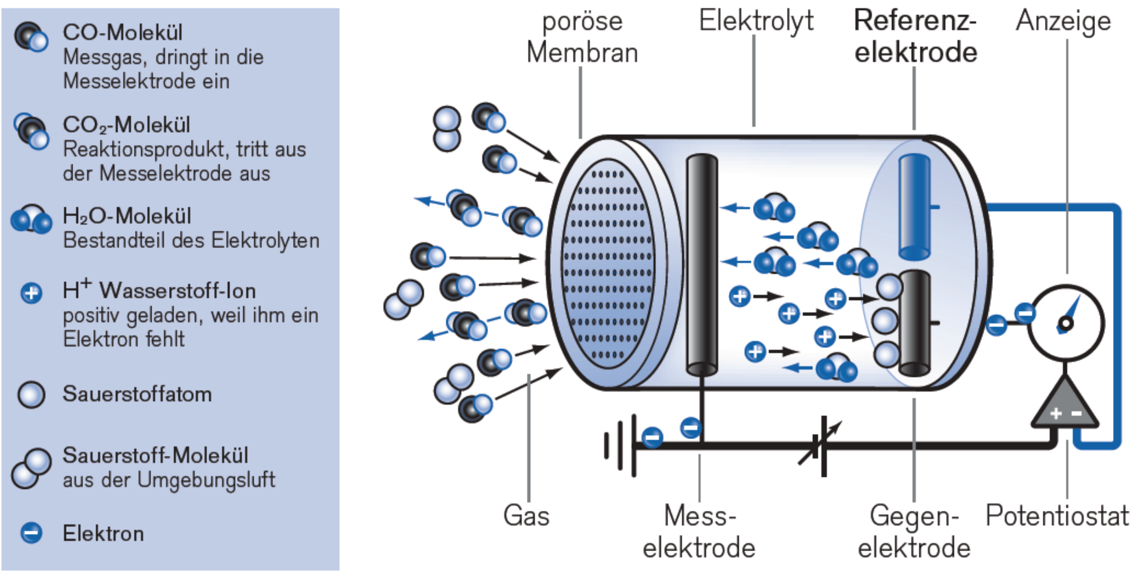
# 2. Example: CO-sensor

If a reducing gas (example: CO) reaches the sensor, it diffuses through the (catalytically active) measuring electrode and displaces its potential in cathodic direction.

An electric current flows through both electrodes because in an acid electrolyte takes place the following reactions:

| | | | |
|---|---|---|---|
| Oxidation of CO (ME) | $2CO + 2H_2O$ | ⇨ | $2CO_2 + 4\,H^+ + 4e^-$ |
| Reduction of $O_2$ (CE) | $O_2 + 4\,H^+ + 4e^-$ | ⇨ | $2H_2O$ |
| Overall reaction: | $2CO + O_2$ | ⇨ | $2CO_2$ |

# 2. Example: CO-sensor




Chemische Reaktion an der Messelektrode

$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

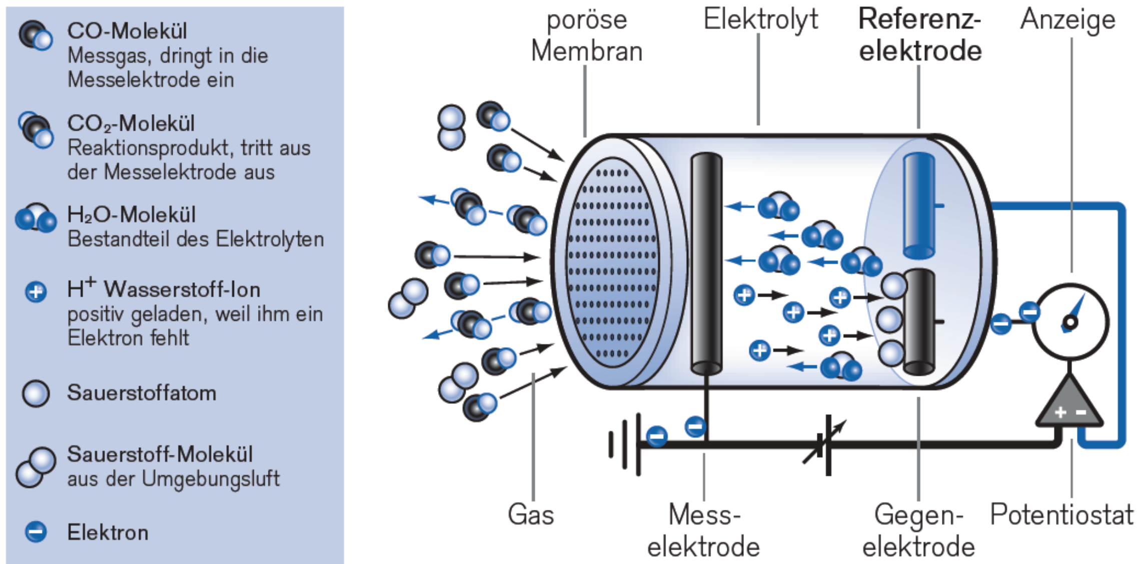
Chemische Reaktion an der Gegenelektrode

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

CO is oxidized to $CO_2$ at the Measuring Electrode after passing through the diffusion barrier , generating $H^+$ ions (protons) and consuming water from the electrolyte. Simultaneously electrons are released from the electrode and reach the counter electrode through the external electric circuit.

The $H^+$ ions move to the counter electrode where, together with the electrons coming from the external circuit and the oxygen dissolved in the surrounding of the electrode, recombine to form water.

# 2. Example: CO-sensor




Chemische Reaktion an der Messelektrode

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Chemische Reaktion an der Gegenelektrode

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$CO_2$ is not absorbed in the acid electrolyte but diffuses back to the ambient.

A supply of oxygen at the counter electrode is necessary to maintain the reaction. Usually this it not a problem because only small amounts of oxygen are consumed and the atmospheric oxygen is in huge amounts.

This is dissolved in the electrolyte and flows to the counter electrode.

# 2. Example: CO-sensor

All electrochemical oxidations in electrochemical sensors (e.g. $H_2S$, CO, NO sensors) rely on the **reduction of oxygen** at the counter electrode, which has be refilled from the atmosphere:

$$O_2 + 4\,H^+ + 4e^- \Rightarrow 2H_2O$$

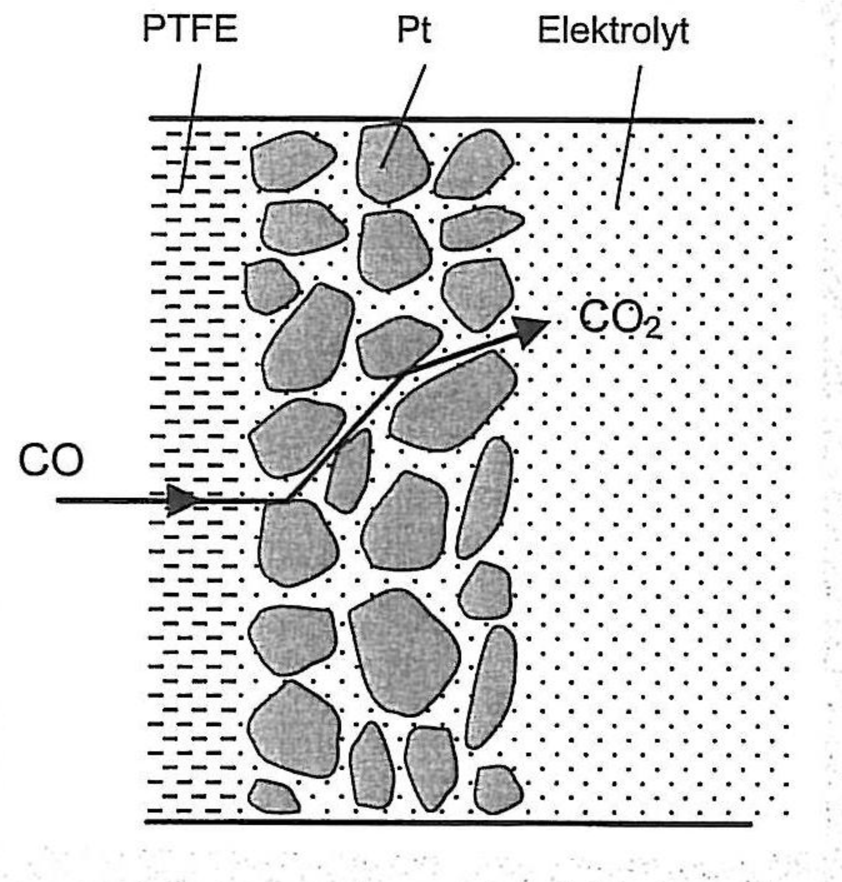
Likewise, most of the sensors based on electrochemical reduction (e.g. $Cl_2$, $NO_2$, $O_3$ sensors) involve the oxidation of water:

$$2H_2O \Rightarrow O_2 + 4\,H^+ + 4e^-$$

# 3. Catalytic electrodes

The electrodes are made from catalytic materials, mostly powder from noble metals (Pt, Pd, Ir, Ag) or graphite powder. The catalysator is deposited on top of an open pored hydrophobic membrane (e.g. PTFE).

In this wasy an electrically conducitive, highly electrolyte-connected surface for reaction gas is formed, known as three-phase boundary. Here is where, really, the required catalytic reactions take place.




Schematical porous Pt electrode and CO reaction.

# 4. Diffusion barriers

The diffusion barrier is very important for establishing an electric current whose value depends on the concentration of the gas. “The sensor cannot be flooded by the reaction components, cannot be saturated”. Depending on the type of sensor and target concentration to be measured, the following diffusion barriers are used:

- Membrane: thin plastic foil through which the gas very slowly flows. Used for high concentrations.
- Capillars: the diffusion through capillars is, generally, independent on the surrounding pressure. Used for high concentrations.
- Porous electrodes on hydrophobic open-pore membranes.

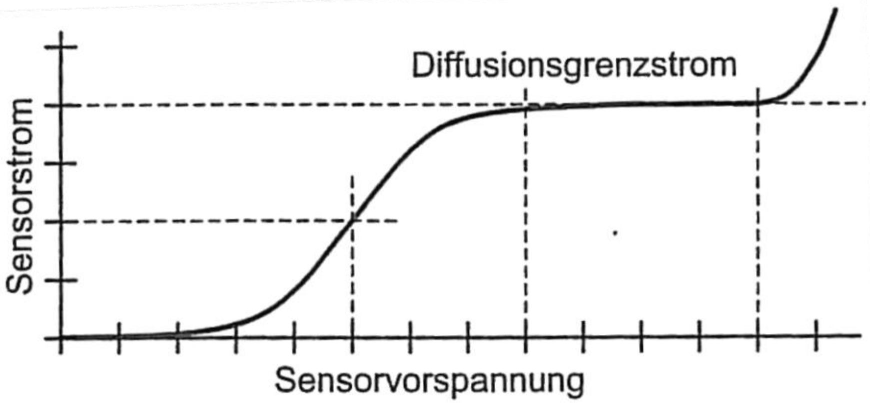
# 4. Diffusion barriers

- It is not easy to find counter electrodes for each target gas that allow the bias of the measuring electrode in such a way that the current-generating reaction takes place. In such cases a reaction can be induced by an external bias.

- Forced anodic reactions: the bias of the measuring electrode needs to be lowered in relation to the counter electrode, which causes a mass exchange and a corresponding current flow. In the counter electrode the known oxygen reduction takes again place.

- A determining point for the development of electrochemical sensors is establishing a diffusion electrode that gives rise to a diffusion current at the specified bias and that the sensor does not "die" in its own reaction products.

# 4. Diffusion barriers



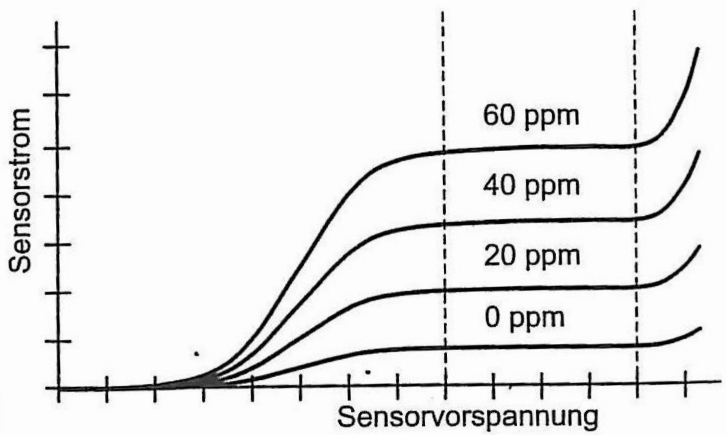




Abb. 25: Ausbildung des Diffusionsgrenzstroms bei unterschiedlichen Gaskonzentrationen

At a given sensor geometry and gas concentration, the sensor current increases first with the voltage between the electrodes and reaches a plateau. The diffusion limiting current is reached and the sensor‘s current is independent from the bias. When the voltage is futher increased starts de electrolysis and the sensor is distroyed.

The plateau is proportionally increased for increasing target gas concentrations.

# 5. Three-electrode sensor and potentiostat

Problem: higher gas concentrations give rise to higher currents and these cause a voltage drop in the sensor.

The voltage drop changes the bias voltage in such a way that, in the worst case, the electrochemical reaction is stopped or occurs differently.

This means that the measured signal is no longer in relation to the gas concentration.

The sensor start to drift or is destroyed by decomposing electrolytic processes.

# 5. Three-electrode sensor and potentiostat

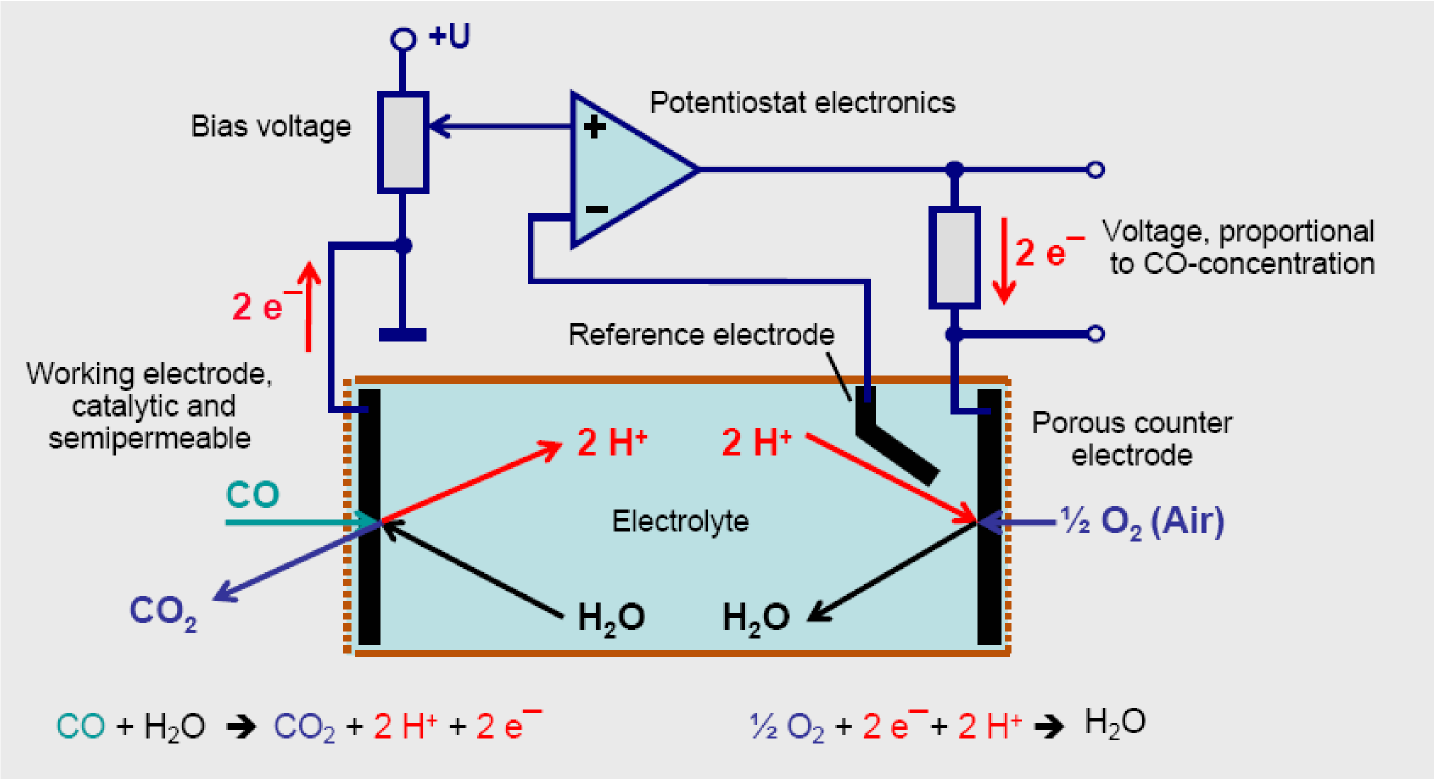
**Help is obtained from a 3rd electrode, the reference electrode.**

**The reference electrode is not circulated by the current and, thus, its potential remains constant.**

**The sensor‘s voltage is monitored continuously through the reference electrode.**

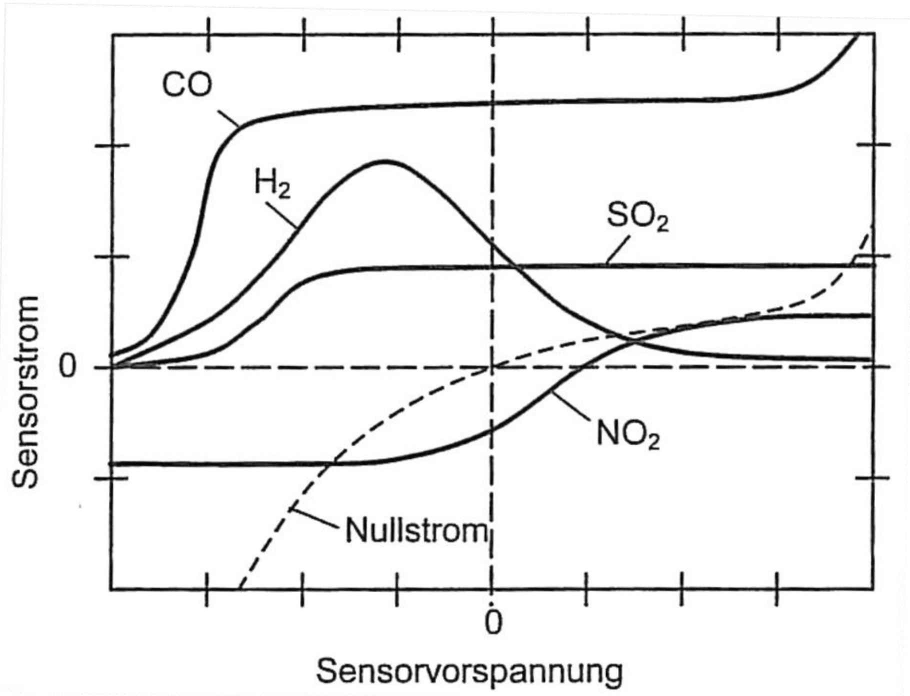
**The sensor‘s voltage changes are corrected by a regulator, i.e., it is kept constant even for different sensor currents.**

# 5. Three-electrode sensor and potentiostat




The regulating magnitude is a current, which is stored in the counter electrode of the so-called potentiostat, that annulates the deviations from the set voltage, so that it is compensated. This current is, at its time, proportional to the gas concentration and can be measured as a voltage dropt at the measuring resistor.

# 5. Three-electrode sensor and potentiostat

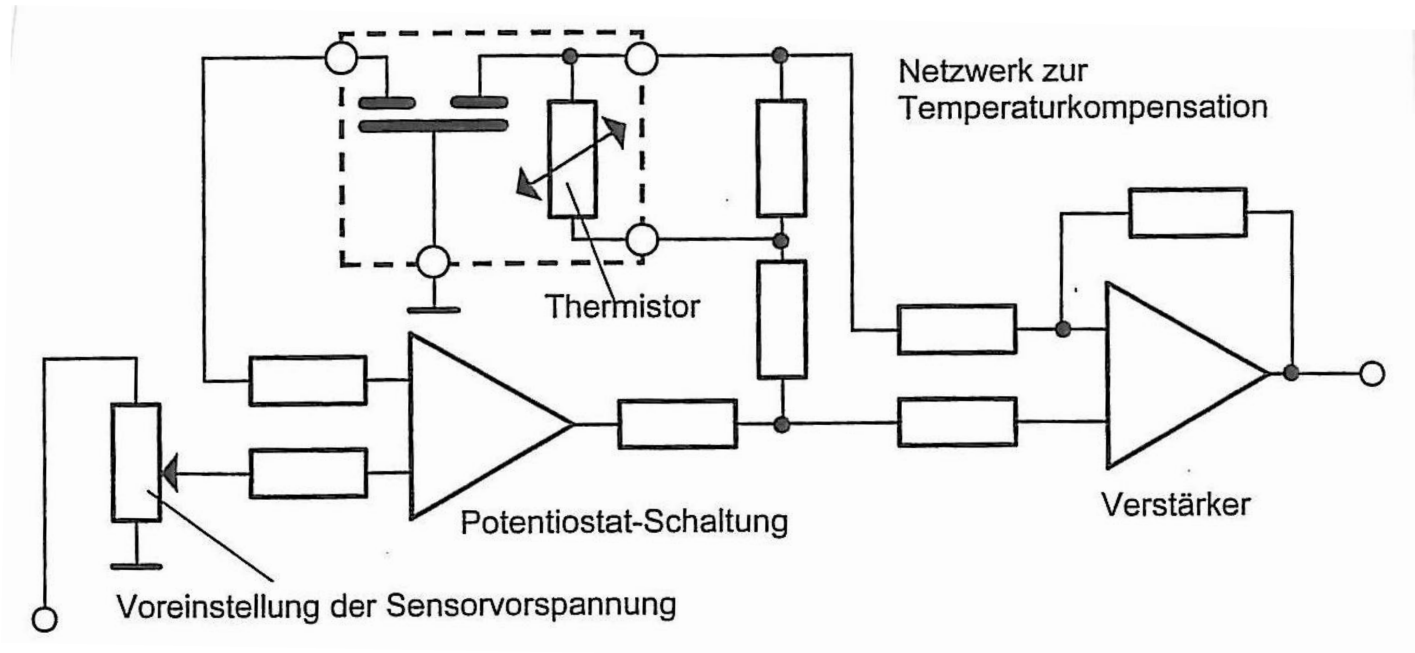



The cross-sensitivity to other gases is strongly influenced by the bias voltage. If in a CO sensor a reduced cross-sensitivity to hydrogen and a positive cross-sensitivity to NO2 is required, then the sensor has to be driven by a positive bias voltage.

A CO sensor with the highest sensitivity would be driven at 0V due to the zero current. However this gives high cross-sensitivity to hydrogen and low to $NO_2$.

# 6. Temperature compensation

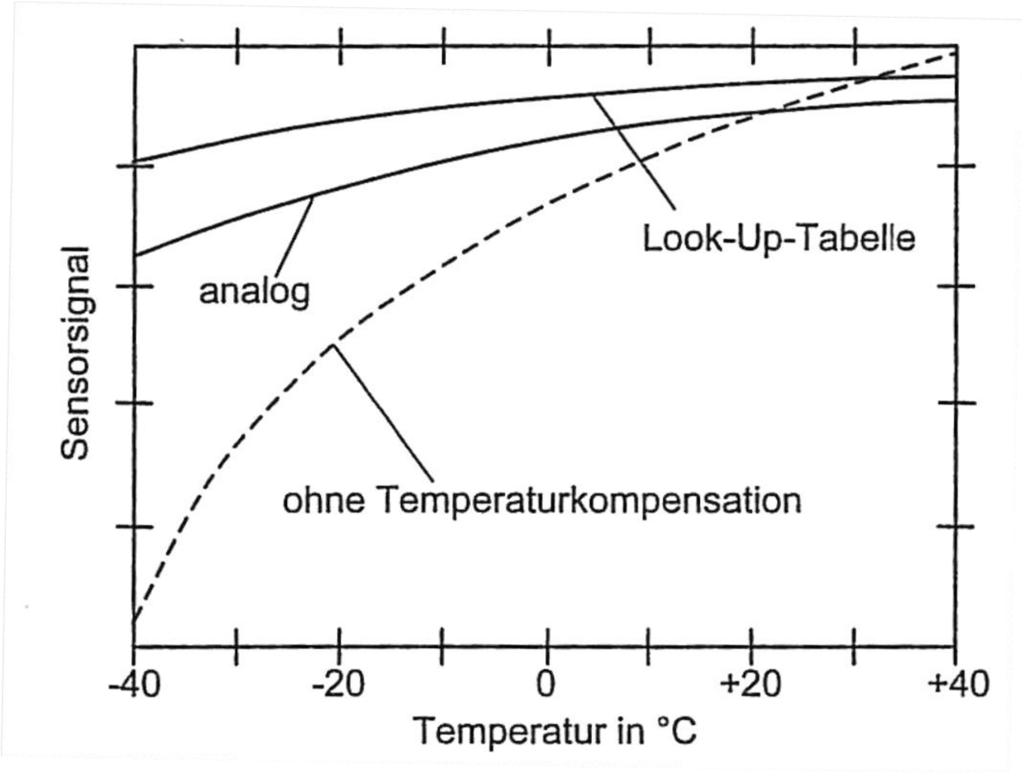
Because both the electrochemical reaction and the diffusion constants are temperature dependent, a continuous monitoring of the sensors temperature is required to correct for temperature variations.




Analog regulator with a thermistor

# 6. Temperature compensation

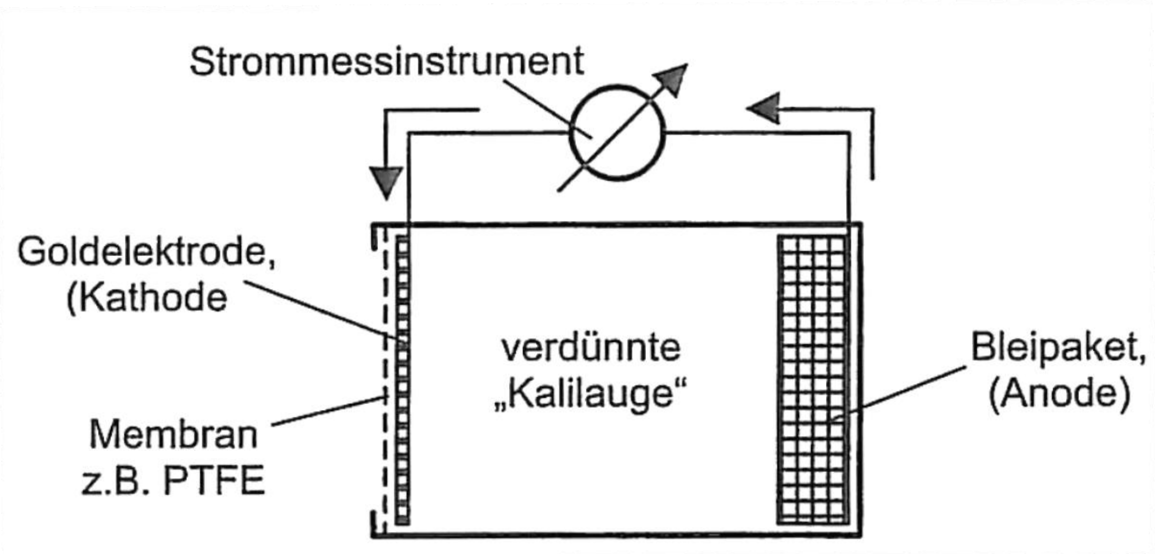
In digital systems the values for compensation are taken from the so-called look-up tables.




Comparison of analog and digital temperature compensation (Dräger)

# 7. Implementation, packages

## Fundamentals of alkaline fuel cells



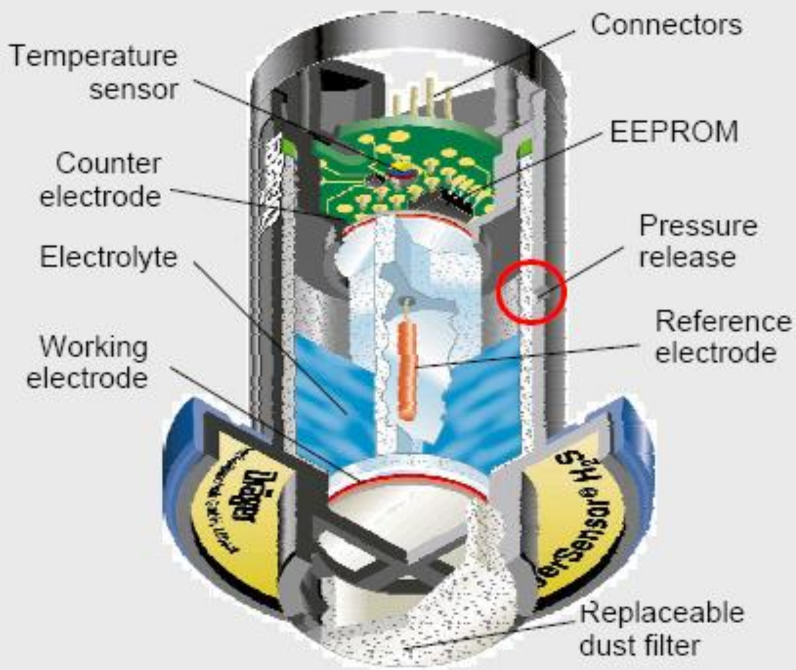

| Basischer Elektrolyt | Gleichung |
|---|---|
| Anode | $2\,H_2 + 4\,OH^- \rightarrow 4\,H_2O + 4e^-$<br>Oxidation / Elektronenabgabe |
| Kathode | $O_2 + 2\,H_2O + 4e^- \rightarrow 4\,OH^-$<br>Reduktion / Elektronenaufnahme |
| Gesamtreaktion | $2\,H_2O + O_2 \rightarrow 2\,H_2O$<br>Redoxreaktion / Zellreaktion |

Here the fuel is lead!

$Pb \rightarrow Pb^{2+} + 2\,e^-$

# 7. Implementation, packages

## MAINSTREAM SENSOR PRINCIPLES
### ELECTROCHEMICAL SENSOR




Polytron 2 with different EC-sensors

The sensor properties can be adjusted and/or optimized for different gases by selection of electrode material, electrolyte composition, and bias voltage.

# 7. Implementation, packages

Tabelle 1: Mit elektrochemischen Sensoren detektierbare Gase und Dämpfe (Auswahl)

| Gas | Formel |
|---|---|
| Acetaldehyd | $CH_3CHO$ |
| Acetylen | $C_2H_2$ |
| Acrylsäure | $C_2H_3COOH$ |
| Ammoniak | $NH_3$ |
| Antimonpentachlorid | $SbCl_5$ |
| Arsenwasserstoff | $AsH_3$ |
| Bortrichlorid | $BCl_3$ |
| Bortrifluorid | $BF_3$ |
| Brom | $Br_2$ |
| Bromwasserstoff | $HBr$ |
| Butadien | $(C_2H_3)_2$ |
| Butylacrylat | $C_2H_3COOC_4H_9$ |
| Butylamin, sec. | $C_4H_9NH_2$ |
| Butylmercaptan, tert. | $C_4H_9SH$ |
| Chlor | $Cl_2$ |
| Chlordioxid | $ClO_2$ |
| Chlortrifluorid | $ClF_3$ |
| Chlorwasserstoff | $HCl$ |
| Cyanwasserstoff | $HCN$ |
| Diboran | $B_2H_6$ |
| Dichlorsilan | $SiH_2Cl_2$ |
| Diethylamin | $(C_2H_5)_2NH$ |
| Diethylamincethanol | $(C_2H_5)_2NC_2H_4OH$ |
| Dimethylamin | $(CH_3)_2NH$ |
| Dimethylsulfid | $(CH_3)_2S$ |
| Epichlorhydrin | $C_2H_3OCH_2Cl$ |
| Ethanol | $C_2H_5OH$ |
| Ethylacrylat | $C_2H_3COOC_2H_5$ |
| Ethylen | $C_2H_4$ |
| Ethylenoxid | $C_2H_4O$ |
| i-Propylamin | $(CH_3)_2CHNH_2$ |
| i-Propylmercaptan | $(CH_3)_2CH_SH$ |
| Kohlenstoffmonoxid | $CO$ |
| Methanol | $CH_3OH$ |
| Methylmercaptan | $CH_3SH$ |
| Methylmetacrylat | $C_2H_2(CH_3)COOCH_3$ |
| Monomethylamin | $CH_3NH_2$ |
| Morpholin | $C_4H_8ONH$ |
| Phosgen | $COCl_2$ |
| Phosphortrichlorid | $PCl_3$ |
| Phosphorwasserstoff | $PH_3$ |
| Phosphorylchlorid | $POCl_3$ |
| Propylen | $C_3H_6$ |
| Propylenoxid | $C_3H_6O$ |
| n-Propylmercaptan | $C_3H_7SH$ |
| Sauerstoff | $O_2$ |
| Schwefeldioxid | $SO_2$ |
| Schwefelwasserstoff | $H_2S$ |
| Selenwasserstoff | $H_2Se$ |
| Silan | $SiH_4$ |
| Siliziumtetrachlorid | $SiCl_4$ |
| Stickstoffdioxid | $NO_2$ |
| Stickstoffmonoxid | $NO$ |
| Tetrahydrothiophen | $C_4H_8S$ |
| Thionylchlorid | $SOCl_2$ |
| Titantetrachlorid | $TiCl_4$ |
| Trichlorsilan | $SiHCl_3$ |
| Triethylamnin | $(C_2H_5)_3N$ |
| Trimethylamin | $(CH_3)_3N$ |
| Trimethylboran | $B(CH_3)_3$ |

Source: Drägerheft 370 (Dezember 1999) – H. Kiesele, M. H. Wittich: Elektrochemische Gassensoren für den Einsatz unter extremen klimatischen Bedingungen



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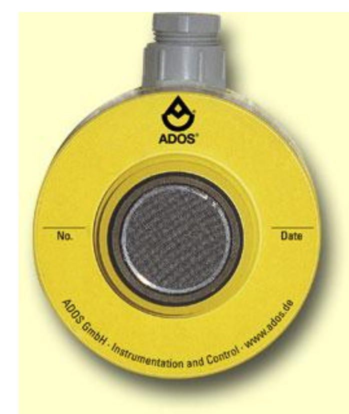
# 7. Implementation, packages



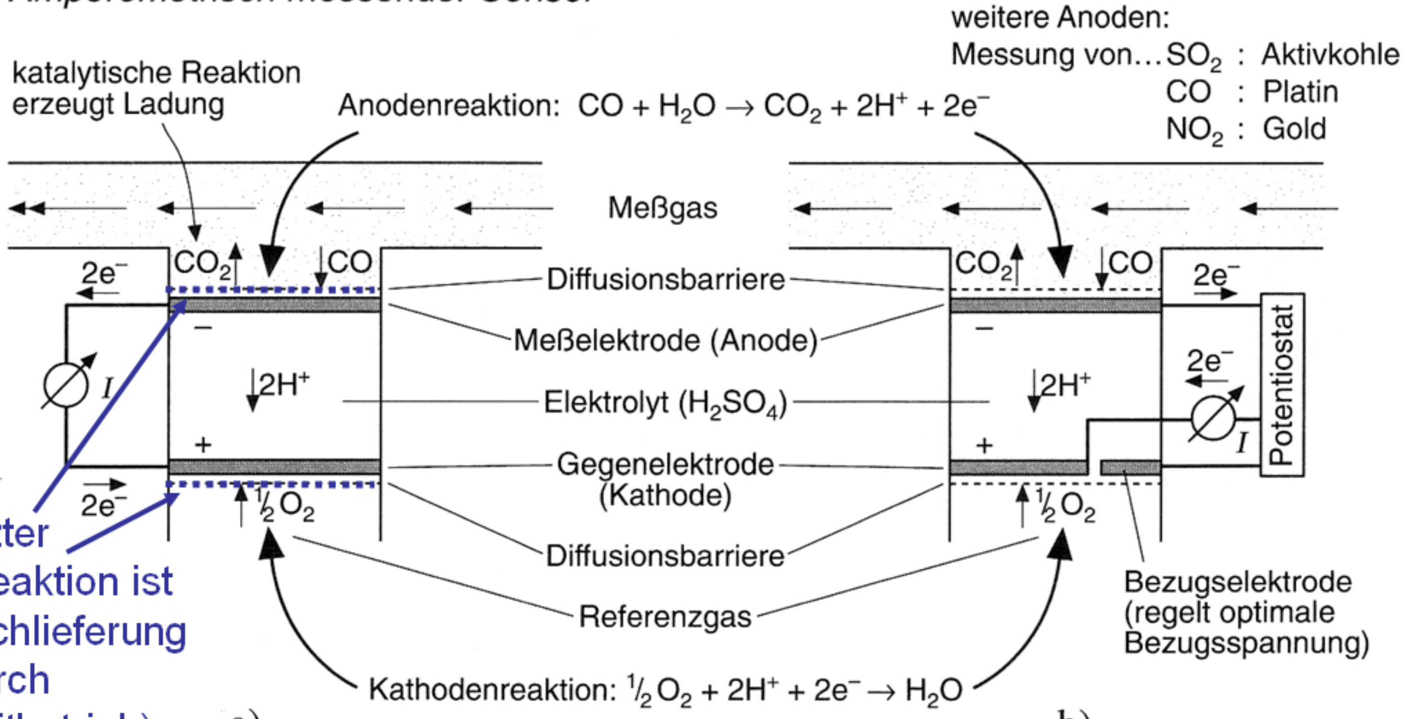



# 7. Implementation, packages

- Gase ionisieren an der Messelektrode, Elektrolyt im Sensorinneren leitet die Ionen durch den Sensor, der entstehende Ionenstrom wird gemessen.
- Selektivität einstellbar durch Elektrolyt, Material der Messelektrode, Potenzial


Quelle: City Technology Ltd.

*Amperometrisch messender Sensor*

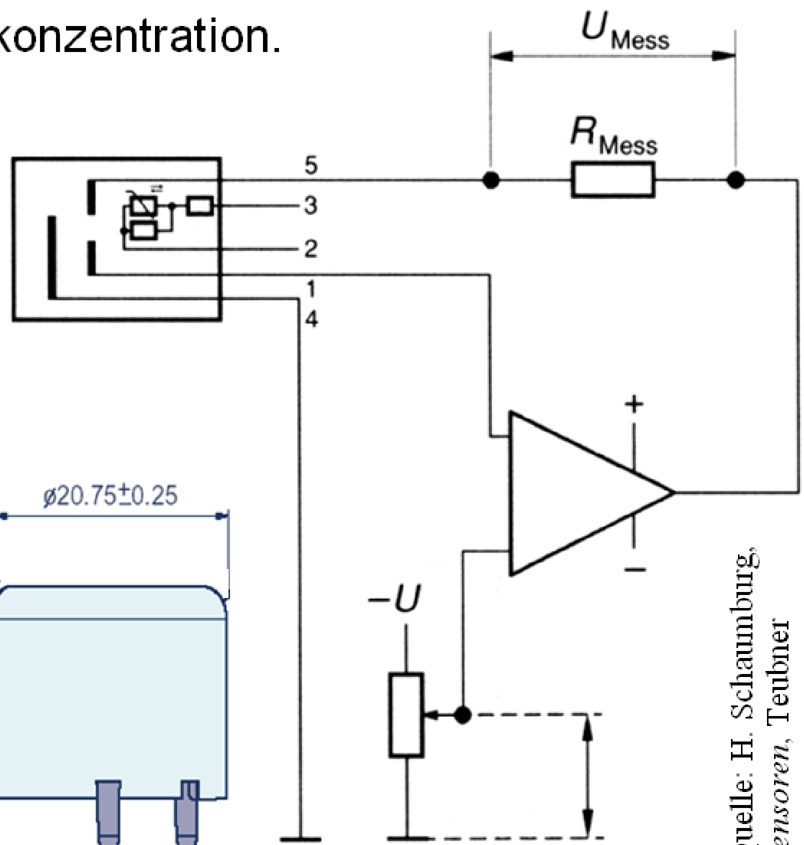



diffusionsbegrenzter Gaszutritt, d.h. Reaktion ist limitiert durch Nachlieferung des Gases (dadurch stabilerer Langzeitbetrieb)

Quelle: H. Schaumburg, *Sensoren*, Teubner

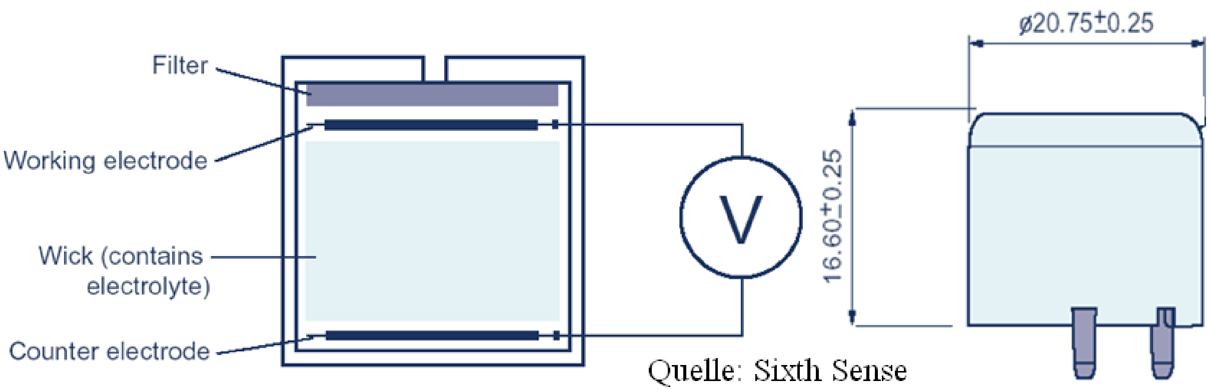
# 7. Implementation, packages

- Durch einen Potentiostaten wird die Spannung zwischen Mess- und Gegen-elektrode konstant gehalten, die Referenzelektrode dient als Bezugspotenzial.
- Der Strom ist dann proportional zur Gaskonzentration.



Quelle: H. Schaumburg, *Sensoren*, Teubner

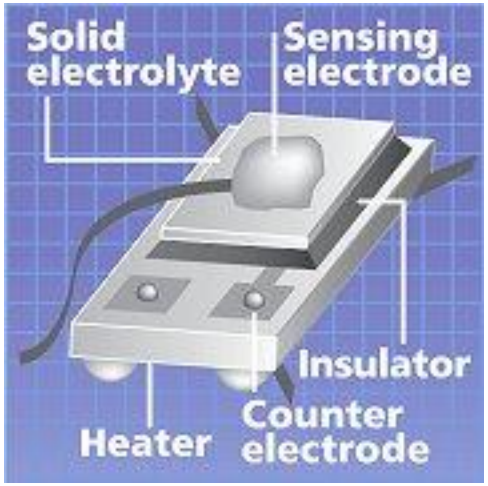
- Einfachere Zellen (unten) arbeiten mit nur zwei Elektroden (Verzicht auf Referenzelektrode), dadurch etwas weniger Temperatur-stabil, aber preiswerter und kompakter.

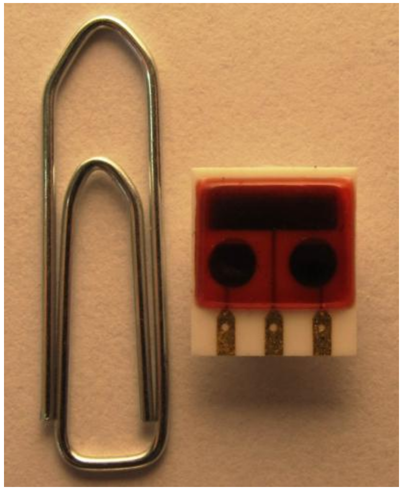


Quelle: Sixth Sense

# 8. Outlook

**Electrochemical cell with polymeric electrolyte**



Quelle: Figaro

**Advantage:** solid electrolyte (no aggressive liquids that can spill out)

**Drawback:** very sensitive to dirt