Chemical sensors based on ceramic materials for pollutant gases detection
A **transducer** is a device, usually electrical or electronic that converts one type of energy to another. Most transducers are either **sensors** or **actuators**.

- In **engineering**, actuators are a subdivision of **transducers**. They are devices which transform an input signal (mainly an electrical signal) into **motion**.
- Electrical **motors**, **pneumatic actuators**, **hydraulic pistons**, **relays**, **comb drive**, **piezoelectric actuators**, and **electroactive polymers** are some examples of such actuators.
**Definition**

- **Sensor, transducer and actuator**

Sensor: is an electronic device that converts a physical, chemical or biological quantity into an electronic signal

*e.g. thermistor*: temperature → electrical resistance

Sensor is a component of an electronic circuit that links a circuitual quantity (current, tension, frequency or phase) to one or more environmental quantities.
Definition

- **Sensors classification** [1]
  - Mechanical;
  - Thermal;
  - Electrical;
  - Magnetic;
  - Radiant;
  - Chemical.

Based on physical principle

Based on quantity to be measured

**Table 1.1: Examples belonging to each class**

**Mechanical**: Length, area, volume, all time derivatives such as linear/angular, velocity/acceleration, mass flow, force, torque, pressure, acoustic wavelength and intensity

**Thermal**: Temperature, (specific) heat, entropy, heat flow, state of matter.

**Electrical**: Voltage, current, charge, resistance, inductance, capacitance, dielectric constant, polarization, electric field, frequency, dipole moment.

**Magnetic**: Field intensity, flux density, magnetic moment, permeability.

**Radiant**: Intensity, phase, wavelength, polarization, reflectance, transmittance, refractive index.

**Chemical**: Composition, concentration, reaction rate, pH, oxidation/reduction potential.
Structure of a generic sensor

- **Receptor**: chemically interactive material. It measures the compound to be detected (measurand).
- **Trasducer**: the measured signal must be sent to the control unit through a trasducer, that makes the data trasmission.
- **Acquisition system**: trasform the signal for the data processing system (if the signal is analogic, it makes the A/D trasformation and send the acquired signal to the data processing system).
- **Data processing system**: makes bit code trasformation.
Definition

Structure of a generic solid-state chemical sensor

- **Environment**
- **Chemically Interactive Material**
- **Basic Device**

- Quantity to be measured (concentration)
- Intermediate quantity
- Electric or optical signal
Definition

environment

cchemically interactive material

Δn

optical interferometer

Δn

Fiber Optic Chemical Sensor

Δm

surface acoustic wave

quartz microbalance

Δm

ΔΦ

ChemFET

MOS capacitor

ΔΦ

kelvin probe

LAPS

interdigitated electrodes

Δσ
**Definition**

*Chemical sensors* can be classified on their applications, as follows:

- volatile compounds (pollutant gases, odours)
- to check liquids (compounds in mineral and sea water)
- DNA sensors
- to recognize nucleic acids (DNA, RNA, PNA)

All of them must recognize **only one compound** in a complex mixture. The sensor response must be reliable and does not be dependent on humidity and temperature, moreover the response time must be fast.
General aspects

- **Sensor parameters** [2]

**Sensitivity**: ratio between the response change of a sensor and the variation of the input.

If the sensor is sensitive to $n$ independent and non-interacting quantities the variation of the output can be expressed as:

$$dV_o = \frac{\partial V_o}{\partial m_1} + \ldots + \frac{\partial V_o}{\partial m_n} = \sum_i \frac{\partial V_o}{\partial m_i} \, dm_i = \sum_i S_i \, dm_i$$
**General aspects**

**Resolution**: the smallest increment in the value of the input that results in a detectable increment in the output. It is expressed as a percentage of the input range.

\[ R_{\text{max}}(\%) = 100 \times \frac{\Delta m_{\text{min}}}{m_{\text{max}} - m_{\text{min}}} \]

**Accuracy**: A measure of how closely the result of the experiment (sensor output) approximates the true value. Since the true value of the unknown is not known a priori, a comparative measurement is needed in specifying the accuracy of a sensor. Inaccuracy is usually described as follows:

\[ \varepsilon_a(\%) = 100 \times \frac{X_m - X_t}{X_t} \]

where \( X_t \) is true value of unknown \( X \), and \( X_m \) is its measured value.

**Precision**: Describes how exactly and reproducibly an unknown value is measured.
**General aspects**

**Selectivity:** In non-ideal sensors, the output might change owing to a change in the environmental parameters or other variables.

**Repeability:** The difference in the output readings at a given value of the input $X$, where $X$ is consecutively reached from $X^-$ (or $X^+$).

**Instability and Drift:** Change of sensitivity or the output level (with zero input) with time, temperature, and any other parameter that is not considered part of the input.
Gas sensors applications

Chemical sensors for detection of pollutant gases are for:

- air monitoring
- combustion control

Main pollutant sources are:

- Industrial working
- Vehicle emissions
- Domestic heating
Pollutant gases [3]

- **Carbon Monoxide** (CO) is a poisonous gas that displaces oxygen from the blood. At high concentrations it is fatal; at lower concentrations, it can exacerbate heart problems.
- **Nitrogen Oxides** (NO\(_x\)) react with hydrocarbons (HC) in sunlight to form ozone and photochemical smog. NO\(_x\) can increase respiratory illnesses and is a contributor to acid rain. Ozone causes breathing difficulties and damages plants.
- **Particulates** are found in the air in a range of sizes. Diesel engines are responsible for the majority of ultra-fine particulates (less than one micron in diameter or PM1). Fine particulates are suspected to be linked to increased rates of premature death.
- **Carbon Dioxide** (CO\(_2\)) is the final product of all combustion processes and the major contributor to the 'greenhouse' effect. Catalysts do not increase overall CO\(_2\) emissions from cars because all the carbon burnt in the engine eventually ends up as CO\(_2\), so CO\(_2\) emissions can only be limited by reducing the amount of fuel used.
- **Unburned hydrocarbons** (HCs) can be formed for different reasons during the combustion process. They cooperate to the formation of photochemical smog and are highly toxic.
- **Sulphur oxides** are particularly toxic for respiratory apparatus.
Exhausts from vehicles

Table 1
Example of exhaust conditions for two- and four-stroke, diesel and lean-four-stroke engines [9,155,176,231]

<table>
<thead>
<tr>
<th>Exhaust components and conditions</th>
<th>Diesel engine</th>
<th>Four-stroke spark ignited-engine</th>
<th>Four-stroke lean-burn spark ignited-engine</th>
<th>Two-stroke spark ignited-engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>350–1000 ppm</td>
<td>100–4000 ppm</td>
<td>≈1200 ppm</td>
<td>100–200 ppm</td>
</tr>
<tr>
<td>HC</td>
<td>50–330 ppm C</td>
<td>500–5000 ppm C</td>
<td>≈1300 ppm C</td>
<td>20,000–30,000 ppm C</td>
</tr>
<tr>
<td>CO</td>
<td>300–1200 ppm</td>
<td>0.1–6%</td>
<td>≈1300 ppm</td>
<td>1–3%</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10–15%</td>
<td>0.2–2%</td>
<td>4–12%</td>
<td>0.2–2%</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.4–7%</td>
<td>10–12%</td>
<td>12%</td>
<td>10–12%</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7%</td>
<td>10–13.5%</td>
<td>11%</td>
<td>10–13%</td>
</tr>
<tr>
<td>SO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>10–100 ppm&lt;sup&gt;b&lt;/sup&gt;</td>
<td>15–60 ppm</td>
<td>20 ppm</td>
<td>≈20 ppm</td>
</tr>
<tr>
<td>PM</td>
<td>65 mg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperatures (test cycle)</td>
<td>r.t.–650 °C (r.t.–420 °C)</td>
<td>r.t.–1100 °C&lt;sup&gt;c&lt;/sup&gt;</td>
<td>r.t.–850 °C</td>
<td>r.t.–1000 °C</td>
</tr>
<tr>
<td>GHSV (h&lt;sup&gt;−1&lt;/sup&gt;)</td>
<td>30,000–100,000</td>
<td>30,000–100,000</td>
<td>30,000–100,000</td>
<td>30,000–100,000</td>
</tr>
<tr>
<td>λ (A/F)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>≈1.8 (26)</td>
<td>≈1 (14.7)</td>
<td>≈1.16 (17)</td>
<td>≈1 (14.7)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> N<sub>2</sub> is remainder.

<sup>b</sup> For comparison: diesel fuels with 500 ppm of sulphur produce about 20 ppm of SO<sub>2</sub> [16].

<sup>c</sup> Close-coupled catalyst.

<sup>d</sup> λ defined as ratio of actual A/F to stoichiometric A/F, λ = 1 at stoichiometry (A/F = 14.7).

<sup>e</sup> Part of the fuel is employed for scavenging of the exhaust, which does not allow to define a precise definition of the A/F.

Typical composition of the exhausts of some internal combustion engines
Exhausts from vehicles

The 1996 European Union regulations reduce the emissions per kilometre from petrol cars by 96% when compared to 1970 levels, with further cuts in 2000 and 2005.

Percentage emissions reduction - Source: European Commission
Exhausts from vehicles

Percentage emissions reduction - Source: European Commission [5]

Reductions in NO\textsubscript{x} and particulate emissions are being introduced for heavy-duty diesel vehicles that are expected to require particulate traps and NOx reduction technologies from 2005.
European Union emission regulations for new light duty vehicles (cars and light commercial vehicles) are specified in the Directive 70/220/EEC. This basis Directive was amended a number of times, some of the most important amendments including:

• Euro 1 standards (also known as EC 93): Directives 91/441/EEC (passenger cars only) or 93/59/EEC (passenger cars and light trucks)
• Euro 2 standards (EC 96): Directives 94/12/EC or 96/69/EC

Euro 2-4 regulations introduce different emission limits for diesel and gasoline vehicles. Diesels have more stringent CO standards but are allowed higher NOx. Gasoline vehicles are exempted from PM standards. Values listed in the following table are type approval emission limits (unless noted otherwise). All dates listed in the tables refer to new type approvals. The EC Directives also specify a second date—one year later—which applies to first registration (entry into service) of existing, previously type-approved vehicle models.
### EU Emission Standards

<table>
<thead>
<tr>
<th>Tier</th>
<th>Date</th>
<th>CO</th>
<th>HC</th>
<th>HC+NOx</th>
<th>NOx</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diesel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1†</td>
<td>1992.07</td>
<td>2.72 (3.16)</td>
<td>-</td>
<td>0.97 (1.13)</td>
<td>-</td>
<td>0.14 (0.18)</td>
</tr>
<tr>
<td>Euro 2, IDI</td>
<td>1996.01</td>
<td>1.0</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>Euro 2, DI</td>
<td>1996.01*</td>
<td>1.0</td>
<td>-</td>
<td>0.9</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>0.64</td>
<td>-</td>
<td>0.56</td>
<td>0.50</td>
<td>0.05</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>0.50</td>
<td>-</td>
<td>0.30</td>
<td>0.25</td>
<td>0.025</td>
</tr>
<tr>
<td><strong>Petrol (Gasoline)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1†</td>
<td>1992.07</td>
<td>2.72 (3.16)</td>
<td>-</td>
<td>0.97 (1.13)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2</td>
<td>1996.01</td>
<td>2.2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>2.30</td>
<td>0.20</td>
<td>-</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>1.0</td>
<td>0.10</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
</tr>
</tbody>
</table>

* Excluding cars over 2,500 kg, which meet N1 Category standards
† Values in brackets are conformity of production (COP) limits.
  a - until 1999.09.30 (after that date DI engines must meet the IDI limits)
Electrochemical gas sensors are devices obtained combining a solid electrolyte (SE) with two electrodes.

Electrochemical sensors are distinguished in:

- **Potentiometric devices**
- **Amperometric devices**

These sensors can be *equilibrium-type* or *non-equilibrium-type*.
Equilibrium potential type

According to the relationship between SE and target gas three types of sensors can be distinguished:

**Type I:** target gas \[\rightarrow\] mobile SE ions

**Type II:** target gas \[\rightarrow\] immobile SE ions

**Type III:** no direct relations without the assistance of an attached auxiliary phase

This classification was firstly introduced for potentiometric electrochemical cell and then used for any type of electrochemical devices.
### Classification of Solid Electrolyte Gas Sensors

<table>
<thead>
<tr>
<th>Type</th>
<th>Cell Structure</th>
<th>Solid Electrolyte</th>
<th>Gas</th>
</tr>
</thead>
</table>
| Type I | $a_A^{ref}$     | $A^+ \xrightarrow{\text{AB}} A$ | $\text{ZrO}_2(\text{+ Y}_2\text{O}_3)$  
$\text{H}_2\text{O}_2\text{O}_3$  
$\text{Sr}_2\text{O}_2 \times \text{H}_2\text{O}$ | $\text{O}_2^{\text{••}}$  
$\text{H}_2\text{••}$  
$\text{H}_2\text{••}$ |
| Type II| $a_A^{ref}$     | $A^+ \xrightarrow{\text{AB}} B$ | $\text{Li}_2\text{SO}_4$  
$\text{Na}_2\text{SO}_3$  
$\text{BaI}_2\text{NO}_3$  
$\text{AgCl}$  
$\text{K}_2\text{CO}_3$  
$\text{SrCl}_2$  
$\text{KCl}$ | $\text{SO}_2^{\text{••}}$  
$\text{SO}_2^{\text{••}}$  
$\text{NO}_2^{\text{••}}$  
$\text{CO}_2^{\text{••}}$  
$\text{Cl}_2^{\text{••}}$ |
| Type IIIa| $a_A^{ref}$ | $A^+ \xrightarrow{\text{AB}} A^+ \xrightarrow{\text{AC}} C$ | $\text{Li}^+$  
$\text{Li}^+$  
$\text{Li}_2\text{CO}_3$  
$\text{LaF}_3$ | $\text{SO}_2^{\text{••}}$  
$\text{SO}_2^{\text{••}}$  
$\text{NO}_2^{\text{••}}$  
$\text{CO}_2^{\text{••}}$  
$\text{O}_2^{\text{••}}$ |
| Type IIIb| $a_A^{ref}$ | $A^+ \xrightarrow{\text{AB}} A^+ \xrightarrow{\text{AC}} C$ | $\text{Li}_2\text{SO}_4$  
$\text{Li}_2\text{CO}_3$  
$\text{LaF}_3$ | $\text{SO}_2^{\text{••}}$  
$\text{SO}_2^{\text{••}}$  
$\text{NO}_2^{\text{••}}$ |
| Type IIIc| $a_A^{ref}$ | $B^+ \xrightarrow{\text{AB}} A^+ \xrightarrow{\text{AC}} C$ | $\text{ZrO}_2(\text{+ MgO})$  
$\text{ZrO}_2(\text{+ MgO})$  
$\text{LaF}_3$ | $\text{SO}_2^{\text{••}}$  
$\text{SO}_2^{\text{••}}$  
$\text{NO}_2^{\text{••}}$  
$\text{CO}_2^{\text{••}}$ |

$^{ref}$: Activity of $A^+$ for the reference electrode  
AB: Solid electrolyte (A $^+$ or B $^-$ conductor)
### Classification

Some examples of potentiometric sensors based on solid electrolytes [6]

<table>
<thead>
<tr>
<th>Type</th>
<th>Cell Structure</th>
<th>Gas Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiometric</td>
<td>(RE) (SE)</td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>$\text{O}_2$, Pt</td>
<td>YSZ</td>
</tr>
<tr>
<td>Type II</td>
<td>CO$_2$+O$_2$, Au</td>
<td>K$_2$CO$_3$</td>
</tr>
<tr>
<td>Type III</td>
<td>O$_2$, Au</td>
<td>NASICON</td>
</tr>
<tr>
<td>Type III</td>
<td>O$_2$, Au</td>
<td>Na$_2$Ti$<em>6$O$</em>{13}$TiO$_2$</td>
</tr>
</tbody>
</table>

RE = reference electrode; SE = sensing electrode.
Classification

Some examples of potentiometric sensors based on solid electrolytes

<table>
<thead>
<tr>
<th>Classification of solid electrolyte gas sensors</th>
<th>Sensing principle</th>
<th>Typical cell structure*</th>
<th>Gas-sensing reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Equilibrium-potential</strong></td>
<td>(RE)</td>
<td>(SE)</td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>O₂,Pt</td>
<td>YSZ</td>
<td>Pt,O₂</td>
</tr>
<tr>
<td>Type II</td>
<td>CO₂ + O₂,Au</td>
<td>K₂CO₃</td>
<td>Au,CO₂ + O₂</td>
</tr>
<tr>
<td>Type III</td>
<td>O₂,Au</td>
<td>NASICON</td>
<td>NaNO₂</td>
</tr>
<tr>
<td>Type III</td>
<td>Au</td>
<td>Na₃O−TiO₃</td>
<td>Na⁺−β-alumina</td>
</tr>
<tr>
<td><strong>Mixed-potential</strong></td>
<td>(RE)</td>
<td>(SE)</td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>O₂,Pt</td>
<td>YSZ</td>
<td>ZnO(Pt),H₂ + O₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2H₂ + O²⁻ → H₂O + 2e⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>½O₂ + 2e⁻ → O²⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO₂ + 2e⁻ → NO + O²⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O²⁻ → ½O₂ + 2e⁻</td>
</tr>
<tr>
<td><strong>Electrochemical pumping</strong></td>
<td>(CE)</td>
<td>(WE)</td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>O₂,Pt</td>
<td>YSZ</td>
<td>Pt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>½O₂ + 2e⁻ → O²⁻</td>
</tr>
<tr>
<td>Type III</td>
<td>O₂ + NO₂,Au</td>
<td>NASICON</td>
<td>NaNO₂</td>
</tr>
</tbody>
</table>

* YSZ: yttria stabilized zirconia (O²⁻ conductor), NASICON: Na₃Zr₂Si₂PO₁₂ (Na⁺ conductor), GDL: gas diffusion layer, RE: reference electrode, SE: sensing electrode, CE: counter electrode, WE: working electrode.
Type I sensors

The most interesting example of type I sensor is the YSZ oxygen sensor with Pt electrodes. It is represented by the following electrochemical cell:

\[ O_2, \text{Pt}^\| \mid \text{YSZ (O}^{2-}\text{-conductor)} \mid \text{Pt}^{\text{II}}, O_2 \]

reference sensing

At the sensing and reference electrodes the same electrochemical reaction occurs:

\[ \frac{1}{2} O_2 + 2e^- (\text{Pt}) \rightleftharpoons O^{2-} (\text{YSZ}) \]
The difference in oxygen partial pressures at the electrodes generates an EMF given by the nernstian equation:

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}^{II}}{p_{O_2}^I}$$

Where $p_{O_2}^{II}$ and $p_{O_2}^I$ are the oxygen partial pressures at side I and II.

*Type I oxygen sensors* are used in many applications: metallurgy, gas production, food and beverage packing, combustion control in furnaces, boilers etc. but the largest use (about 75%) is in automobiles (*lambda sensor*).
Lambda probe

Scheme of oxygen sensor

Scheme of lambda probe

Commernial lambda probe from Bosch
Type II sensors

Metal salts of oxyacid (modest conductors of cations) can serve as SE membranes for oxidic gas sensor, i.e. K₂CO₃ for CO₂, Ba(NO₃)₂ for NO₂ and Na₂SO₄ for SO₂.

For a CO₂ sensor the electrochemical cell is given by a K₂CO₃ disk:

\[
\text{CO}_2\text{-O}_2, \text{Au}^{\text{I}} \frac{1}{2} \text{K}_2\text{CO}_3 \frac{1}{2} \text{II} \text{Au}, \text{CO}_2\text{-O}_2
\]

K₂CO₃ behaves as a K⁺ solid electrolyte conductor.

At both electrodes the electrochemical reaction is the following:

\[
2\text{K}^+ + \text{CO}_2 + \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{K}_2\text{CO}_3 \text{ (solid)}
\]

leading to a concentration cell for O₂ and CO₂. The EMF of the device is:

\[
E = \frac{RT}{2F} \ln \left( \frac{P^{\text{II}}_{\text{CO}_2} \left( P^{\text{II}}_{\text{O}_2} \right)^{1/2}}{P^{\text{I}}_{\text{CO}_2} \left( P^{\text{I}}_{\text{O}_2} \right)^{1/2}} \right)
\]
Type III sensors

the use of oxyacid salts as AP in combination with a typical SE has been proposed.

Proposed electrochemical cell for CO$_2$ detection:

$CO_2$-aria, Au$^{\|}$|NASICON|$^{\|}$ Au, Na$_2$CO$_3$, CO$_2$-aria

Reference electrode: $Na_2O$ (NASICON) $\rightleftharpoons$ $2Na^+ + \frac{1}{2} O_2 + 2e^-$

Sensing electrode: $2Na^+ + CO_2 + O_2 + 2e^- \rightleftharpoons Na_2CO_3$

Overall reaction: $CO_2 + Na_2O$ (NASICON) $\rightleftharpoons Na_2CO_3$

The EMF of the cell is:

$$E = E_0 + \frac{RT}{2F} \ln P_{CO_2}$$

$E_0$ is constant for fixed T and Na$_2$O activity.
Type III sensors can be divided in three subtypes according to the relation between the mobile ion of the solid electrolyte (SE) and the auxiliary phase (AP):

Type III a: SE and AP have the same mobile ions (i.e., NASICON and Na$_2$CO$_3$)

Type III b: SE and AP have different mobile ions with the same sign

Type III c: SE and AP have different mobile ions with different sign

A mediating layer (ionic bridge) between SE and AP is necessary in type III b and III c sensors. In many cases it forms spontaneously.
Type III sensors have increased the degree of freedom in sensor design and materials selection dramatically. Moreover, instead of oxyacid salts, multicomponent system can be used as AP which can improve the sensing and mechanical properties of the devices.

Main limitation: thermal and chemical stability of the oxyacid salts.
Typical structure of type III sensors:

a) Tubular device supported by a glass tube;
b) SE tubular device;
c) Planar device.

SE = solid electrolyte; AP = auxiliary phase
**Type III gas sensors performances**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solid electrolyte</th>
<th>Auxiliary phase</th>
<th>T(°C)</th>
<th>Response time (s) (90%)</th>
<th>Range of concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>NASICON</td>
<td>Na₂CO₃·BaCO₃, Li₂CO₃·CaCO₃, Li₂CO₃·BaCO₃</td>
<td>550</td>
<td>&lt; 8</td>
<td>4 ppm–40%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>&lt; 8</td>
<td>4 ppm–40%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>270</td>
<td>60</td>
<td>4 ppm–40%</td>
</tr>
<tr>
<td>NO₂</td>
<td>NASICON</td>
<td>NaNNO₃, NaNO₂, NaNNO₂·Li₂CO₃</td>
<td>150</td>
<td>60</td>
<td>1–200 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150–225</td>
<td>&lt; 8</td>
<td>0.1–200 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>&lt; 8</td>
<td>0.0005–200 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>NASICON</td>
<td>NaNNO₂</td>
<td>150–225</td>
<td>&lt; 8</td>
<td>1–800 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>MgO stabilized Zirconia</td>
<td>Li₂SO₄·CaSO₄, Li₂SO₄·CaSO₄·S iO₂</td>
<td>700</td>
<td>&lt;10</td>
<td>2–200 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650</td>
<td>&lt;10</td>
<td>2–200 ppm</td>
</tr>
</tbody>
</table>
Type III sensors

EMF of NO₂, SO₂, and CO₂ sensors vs gas concentration. The AP/SE combination used and the number of electrons involved in the electrode reaction per gas molecule are reported: a) NO₂ (150°C), b) SO₂ (650°C), c) CO₂ (500°C).
• Electrodes based on Rh, Pd or their alloys with Pt behave as equilibrium electrodes in presence of CO, HCs and NOx. On the other hand, Au, Ag, Bi, Pb, or their alloys with Pt do not have catalytic properties for CO, HCs and NOx, and behave as equilibrium electrodes at high temperatures and as mixed potential electrode at lower temperatures.

• Sensors with electrodes based on Pt/Au alloy, show better response to CO and H$_2$, at temperature of 550°C [32]. This behavior is probably due to the decreasing of the catalytic activity of the alloy in the H$_2$ and CO oxidation.
In the figure the YSZ potentiometric sensor for H₂ detection is reported. This is an oxygen sensor with the sensing electrode with a porous layer of ZnO. The sensor shows an high response to H₂ in air in the temperature range 450-600°C. The substitution of Pt with ZnO increases the working temperature up to 600°C. The sensor with Pt sensing electrode does not work at 500°C. The FEM is linear with the logarithm of H₂ concentration even if the slope is not consistent with a nernstian behavior. The EMF decrease with the increasing of temperature can be explained with the increasing of the catalytic oxidation of H₂ with temperature. Moreover this sensor has a good selectivity even in presence of NO, NO₂, CH₄, CO₂ and H₂O and good stability.

(a) H₂ sensor based on YSZ and ZnO electrode (b) EMF at different temperatures vs H₂ concentration[52].
Pt/metal oxide electrodes

Sensori di CO2 con elettrodo sensibile di ossido

Normalmente per la rilevazione di CO2 si utilizzano sensori di tipo III a base di NASICON con fasi ausiliarie di carbonati. Recentemente Bredikhin e Weppner hanno dimostrato la possibilità di accoppiare NASICON con un semiconduttore a base di SnO2 (drogato con Sb) per la rilevazione di CO2. Questo sensore ha mostrato buone proprietà di rilevazione e tempi di risposta veloci anche a temperatura ambiente.

Vari ossidi di tipo perovskitico sono stati utilizzati per la preparazione dell'elettrodo sensibile in dispositivi potenziometrici a base di NASICON che operano con aria di riferimento. Tra gli ossidi perovskitici sperimentati per la preparazione dell'elettrodo sensibile, quelli che hanno mostrato le proprietà di rilevazione migliori nell'intervallo di temperature 200-300°C sono delle cobaltititi, in particolar modo NdCoO₃ e La₀.₈Ba₀.₂CoO₃. Per spiegare la dipendenza della risposta del sensore dal particolare tipo di ossido utilizzato, Shimizu et al. propongono una diversa attività elettrocatalitica e/o un diverso comportamento di adsorbimento-desorbimento del gas da parte dell'elettrodo di ossido.