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Electro-chemical gas sensor for multi-gas detection application

J. Kathirvelan
MEMS & Sensors Division, SENSE, VIT University, Vellore, Tamilnadu-632014, India
j.kathirvelan@vit.ac.in

Abstract

In the recent past, there is a tremendous need for automotive exhaust emission monitoring and air quality monitoring (Indoor). The existing gas sensors can detect only single gas at a time and sensor arrays are being used for multi-gas detection application which has many drawbacks like poor accuracy, bulky circuit, non-reliable, costlier and etc. To overcome the drawbacks of the existing sensor arrays, there is a need to develop a novel gas sensor using advanced developments in the sensor fabrication and with new electrode and electrolyte materials. So there is a tremendous need for developing a gas chromatography instrument with a single sensor element in order to have cost effectiveness, compact, linear, good accuracy and reliable.

Keywords: Solid electrolyte (YSZ), multi-metallic electrodes, multi-gas detection, Cyclic Voltammetry, Voltammogram.

Introduction

The most dangerous air pollutants are nitrogen monoxide (NO) and Nitrogen dioxide (NO_2) collectively referred as NOx. These gases can produce health hazards. The off-road engines contribute about a half of NOx emissions from combustion engines (Serge Zhuiykov & Norio Miura, 2007).

Optimization of engine combustion process has already lowered NOx emissions significantly (Serge Zhuiykov & Norio Miura, 2007). Ultra lean-burn engine system has been developed recently to improve fuel efficiency and also to reduce NOx and CO_2 emission.

Table 1. EU emission standards for HD diesel engines

Phase of standard	Year	NO_x (g/kWh)
Euro III	2000	5.0
Euro IV	2005	3.5
Euro V	2008	2.0

Table 1 illustrates the European limits for NOx emissions applied on-road engines. The new advanced engine system and positions of different sensors are shown in the Fig.1. and also the market trends of automotive exhaust gas sensors is shown in the Fig.2.

Fig.1. New advanced engine system and positions of different sensors [source: Serge Zhuiykov & Norio Miura, (2007) *with permission from Elsevier Sciences]*

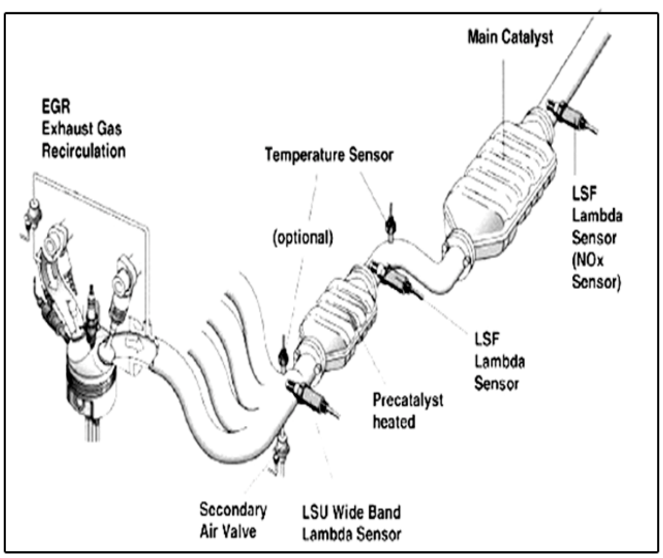
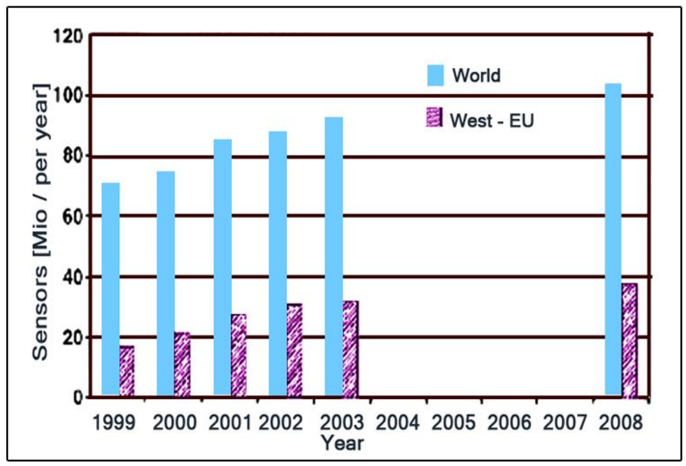


Fig.2. Market trends of automotive exhaust gas sensors [source: Serge Zhuiykov & Norio Miura, (2007) *with permission from Elsevier Sciences]*



The requirements for NOx sensor used in the commercial combustion application are mentioned in (Serge Zhuiykov & Norio Miura, 2007) and those are: a). It should withstand high temperatures (600-900^{o}C) for a long time as it should be placed very close to the engine for fast response, b). The output of the sensor should be insensitive to the moisture content, c). In the absence of oxygen, the sensor should provide stable signals, and d). The sensor should be inexpensive.

In the recent past, surplus number of research work has been carried out to find out the gases present in the gas mixture using solid state electrochemical sensors but unfortunately all the research works are limited only with the detection of single gas.

The latest research work carried out with solid electrolyte [YSZ] and multi-metalic electrode combination by (Schmidt *et al*., 2000) using amperometric technique could able to detect only the gases present in the binary gas mixture O_2, N_2 and NO, N_2. In continuation to this existing work, a new research work has been proposed to carry out the detection of multi-gases present in the automotive exhaust with solid electrolyte based

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electrochemical gas sensor using cyclic Voltammetric technique.

Work status on gas sensor over four decades

Quite number of research on solid electrolyte based electrochemical gas sensors has been made in the last four decades (Chand & Cunningham, 1970; Sedlak & Blurton, 1976; Fleming William, 1977; Stetter *et al*., 1986; Werener Weppener, 1987; Deublein *et al*., 1988; Gayet & YU, 1988; Katsuhiko, 1991; Reinhardt *et al*., 1995; Somov *et al*., 1995; Serguei *et al*., 1996; Shoemaker *et al*., 1997; Pijolt *et al*., 1999; Schmidt *et al*., 2000; Serge *et al*., 2001; Jasinski, 2006; Serge Zhuiykov & Norio Miura, 2007; Ralf *et al*., 2009; Yu *et al*., 2010). Most of the research works were based on the YSZ solid electrolyte. Almost all the research was carried out using one of these techniques: Potentiometric, Amperometric and Conductometric and Electrocatalytic types.

Most of the research works were carried out using either single electrode setup or multi-electrode setup and also at different operating temperatures for the separation of the electrode reactions. All the research works are limited with detection single gas for different applications. Most of the research works focused on the detection of combustible gases for the emission monitoring and for the air quality monitoring.

Electrochemical sensor

Fig.3 represents the conventional electro-chemical sensor unit. The Electrochemical Sensor is used to convert the reactions occurring between the electrode surface and the analyte in the electrolyte into electrical signals.

Different types of Electro-chemical Sensors

Potentiometric sensors: Potentiometric sensors consist of a solid electrolyte and two electronically conducting electrodes. The EMF of the sensor measured in this method will follow the Nernst equation (1) (Jasinski, 2006).

Fig.3. Conventional electrochemical sensor unit

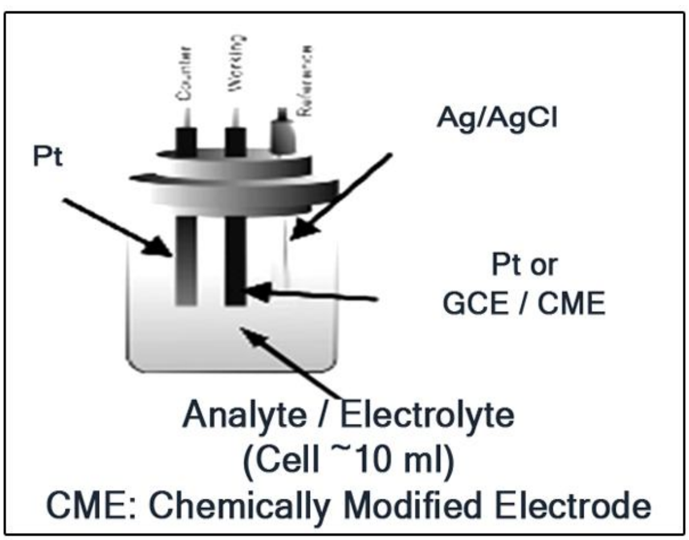
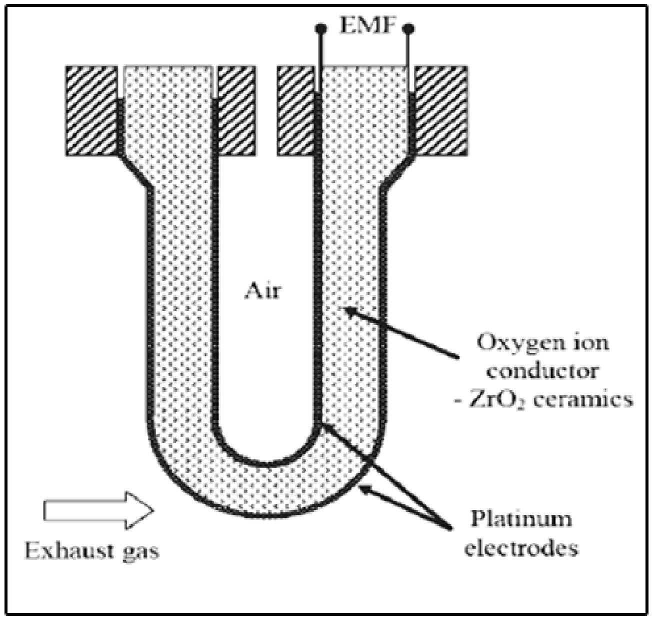


Fig.4. Simplified schematic diagram of an unheated thimble-type oxygen sensor



$$\text{EMF} = E_0 + \frac{RT}{nF}\ln\frac{P_w}{P^0} \quad \text{------(1)}$$

Where, E_o is the EMF at a standard pressure of 1 bar, R- the gas constant, F- the Faraday constant, n- the number of electrons involved in the reaction of the gas molecule, T- the absolute temperature, P_w is the gas partial pressure at the working electrode and P^o is the standard pressure (1 bar).

The example for potentiometric sensor is the lambda sensor used in the stoichiometric-burn engines to control the air-fuel ratio. The construction of the Lambda sensor is presented in Fig.4.

The oxygen molecules equilibrate at the interface of the electrolyte and platinum electrode, in accordance with the following electrochemical reaction:

O_2 (gas) + $4e^-$ (electrode) $\longrightarrow$ $2O^{2-}$ (electrolyte)---------- (2)

The EMF of the sensor will be about 0.9V when the air-to-fuel mixture is rich and during lean burn, it will be about 0.1V (Jasinski, 2006).

Amperometric sensors: Amperometric sensors will provide a linear dependence of the electrical signal on gas concentration. It has small temperature sensitivity and lack of any reference electrode. Amperometric sensors are widely used in controlling the operation of lean-burn engines (Jasinski, 2006).

A typical structure of an amperometric oxygen sensor with a hole as the diffusion barrier is presented in Fig.5. The following electrochemical reaction occurs at the cathode (negative terminal) when an external voltage is applied

O_2 (gas) + $4e^-$ (electrode) $\longrightarrow$ $2O^{2-}$ (electrolyte----------(3)

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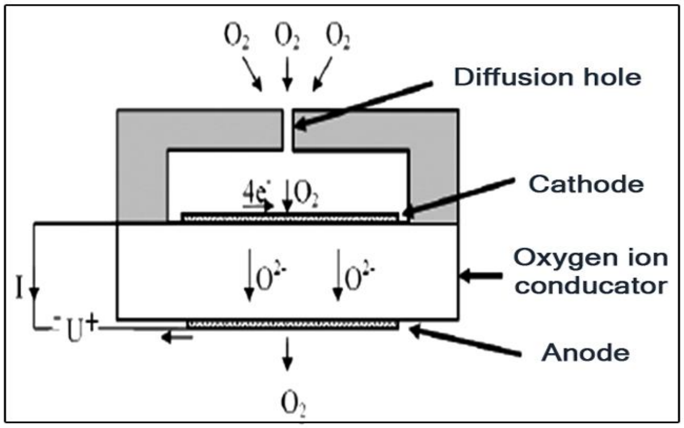
The oxygen ions moving across the electrolyte to the anode will recombine to give oxygen molecules in an ambient gas.

$2O^{2-}$(electrolyte) ⟶ O_2 (gas) + $4e^-$(electrode) --------(4)

The limiting current is given by following equation:

$$I_{lim} = -\frac{nFD_{o_2}AP}{RTL}\ln(1-x_{o_2}) \quad \text{--------(5)}$$

Fig.5. Design and sensing mechanism of an amperometric oxygen sensor with a hole as the Diffusion barrier



Where, n is the number of electrons involved in the reaction, F is the Faraday constant, Do2 is the diffusion coefficient of gaseous O_2, A is the area of the diffusion hole, P is barometric pressure, R is the gas constant, T is the operating temperature, L- the length of the diffusion hole, and Xo_2- the oxygen mole fraction.

Electrocatalytic sensors: A voltage or current excitation is used in electrocatalytic gas sensors. This type of sensor will provide more information over the conventional potentiometric or amperometric electrochemical sensors (Jasinski, 2006).

Fig.6. Structure of the electro-catalytic gas sensor based on Lisicon solid electrolvte

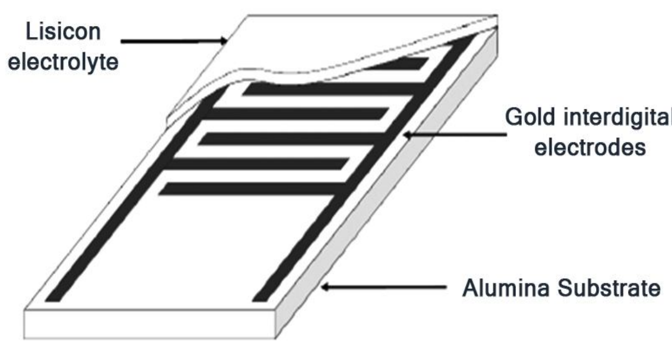


Fig.6 presents the structure of an electrocatalytic sensor based on Lisicon solid electrolyte.The principal of operation of this sensor is based on the excitation of the sensor with a periodic signal. Usually, a triangular voltage is used as the excitation signal, while an electric current is recorded.

The positions and heights of peaks in the current-voltage plot obtained in this way depend on the gas type and concentration. The working principle is similar to cyclic voltammetry, which is used in liquid electrochemistry for, e.g., detecting traces of heavy metals in water (Jasinski, 2006).

Binary gas sensor using multi-metallic electrodes and YSZ solid electrolyte

Pt/YSZ, PtAu/YSZ and RhPtAu/YSZ thick film electrodes in O_2, N_2 and NO, N_2 gas mixtures at high temperatures were investigated by electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) (Schmidt *et al*., 2000).

As compared with the Pt/YSZ electrode the cathodic O_2 reduction at both multi-metallic electrodes is strongly withdrawn , which confirms that the charge transfer resistance for cathodic O2 reduction as follows: *R*ct(Pt/YSZ) < *R*ct(PtAu/YSZ) < *R*ct(RhPtAu/YSZ).

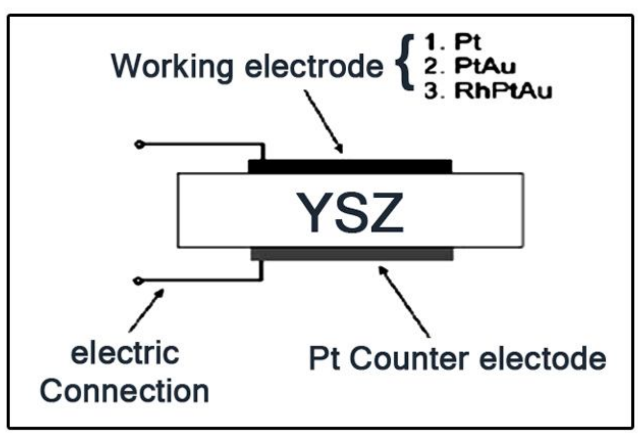
In contrast to that the cathodic NO reduction is enhanced only by the RhPtAu/YSZ electrode, indicating that the RhPtAu mixture is a suitable working electrode material for amperometric NO sensors based on the solid electrolyte (YSZ).

A new amperometric NO sensor with only one working electrode made of RhPtAu mixture was tested in simulated gas mixtures containing NO, O_2, N_2, resulting in a linear response to the NO concentration, which is nearly independent of the O2 concentration (Schmidt *et al*., 2000).

The development of these sensors is faced with the general problem of the cross sensitivity of the NO sensitive electrode towards oxygen. Hence amperometric NO gas sensors usually will have at least two working electrodes: the oxygen pumping electrode (OPE) and the NO detection electrode (NODE) where the NO concentration is measured in an essentially oxygen free gas mixture.

For oxygen pumping from the sensor the Pt/YSZ electrodes are mainly used due to their high catalytic

Fig.7. Electrochemical electrode test cell for EIS and LSV measurements [source: Schmidt-Zhang *et al*. (2005)*with permission from Elsevier Sciences]*



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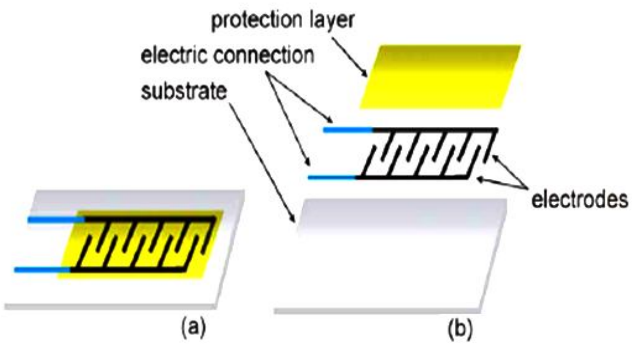
activity for the O_2 reduction (Schmidt *et al*., 2000).

The NO cross-sensitivity of the OPE can be suppressed by modifying the Pt/YSZ electrode with additional metals or metal oxides. Alternatively, it is possible to design sensors without OPE, if NODEs with negligible O_2 sensitivity and high NO sensitivity are available.

Fig.8. Amperometric NO gas sensor design (a) complete sensor;(b) sensor components. [source: Schmidt-Zhang *et al*. (2005)*with permission from Elsevier Sciences]*



For this purpose multi-metallic PtAu/YSZ and RhPtAu/YSZ electrodes were studied and compared with the Pt/YSZ electrode, employing electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). Fig.7 represents the new model electrode test cell for the Electron impedance spectroscopy and Linear sweep Voltammetry. Fig.8 represents the explode view of NO gas sensor developed by using thick film technology.

Fig.9. Electrochemical impedance spectra for three different electrodes exposed to the O_2, N_2 gas mixture containing vol.% at 600^oC, U=0mV [source: Schmidt-Zhang *et al*. (2005)*with permission from Elsevier Sciences]*

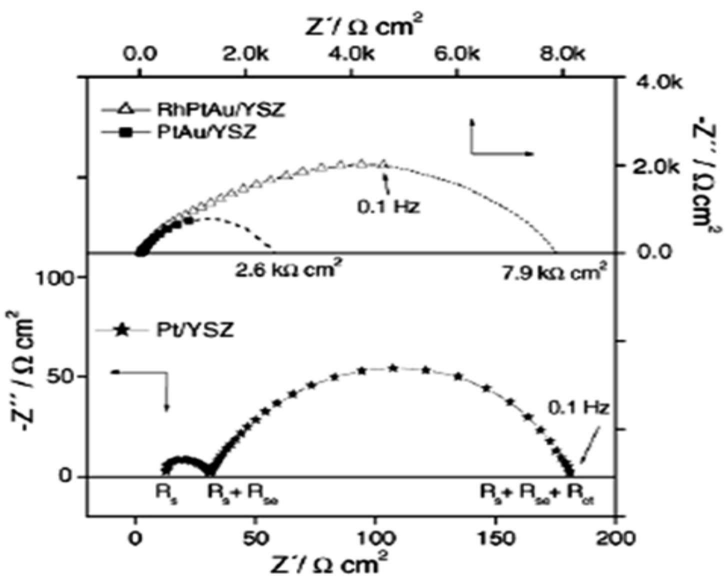


Fig.10. j-U curves (Current density Vs Potential) for the three different electrodes exposed to 1 vol.% O_2, N_2 gas mixture at 600 °C [source: Schmidt-Zhang *et al*. (2005)*with permission from Elsevier Sciences]*

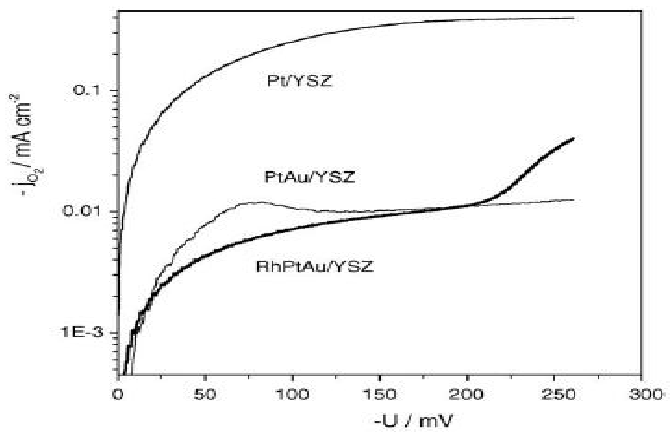


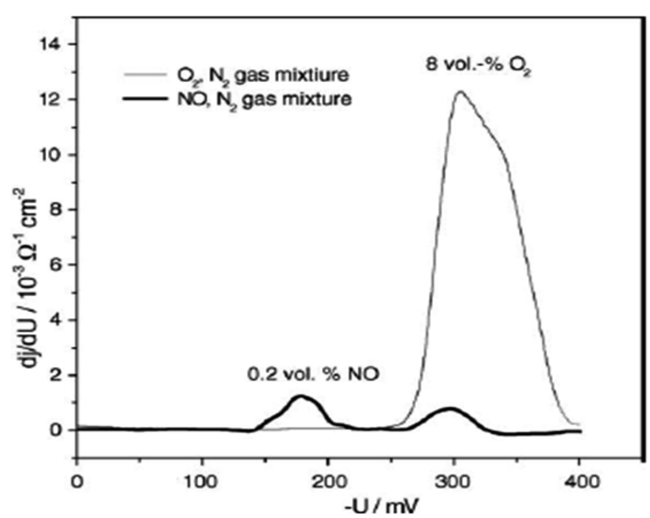
Fig.9 represents the electrochemical impedance spectra for the different electrodes exposed to O2, N2 gas mixture. From the EIS measurements the order established for cathodic O_2 reduction can be: Rct(Pt/YSZ) < Rct(PtAu/YSZ) < Rct(RhPtAu/YSZ).

The inhibitor effect is also confirmed by *j-U* curves (Current Density Vs Potential), given in Fig.10. with the order of current densities (j) for the potential region 0 >U > −200mV.

$|jO_2$ (Pt/YSZ)|> $|jO_2$(PtAu/YSZ)|> $|jO_2$(RhPtAu/YSZ)|

The LSV measurements were performed at the RhPtAu/YSZ electrodes in binary O_2, N_2 and NO, N_2 gas mixtures, respectively. The obtained linear sweep voltammograms (LSVG) Fig.11 shows one reduction step for O_2, N_2 gas mixtures but *two* reduction steps for NO, N_2 gas mixtures. The first peak is attributed to the NO

Fig.11. Derivative linear sweep voltammograms of the RhPtAu/YSZ electrode exposed to 8 vol.% O_2, N_2 and 0.2 vol.% NO, N_2 gas mixtures, respectively, at 550 °C [source: Schmidt-Zhang *et al*. (2005)*with permission from Elsevier Sciences]*



reduction and the second one to the O_2 reduction, respectively. No peak appears at potentials between −250 U<0mV.

In O_2, N_2 gas mixtures and dj/dU converges to zero, e.g. Rp tends to infinity because dj/dU corresponds to the reciprocal of the polarisation resistance Rp.

This means that in this potential range the RhPtAu/YSZ electrode is not polarisable for O_2 reduction. In contrast to that behaviour the RhPtAu/YSZ electrode is very active for NO reduction confirmed by the sharp peak at about −180mV in the NO, N_2 gas mixture.

Hence RhPtAu/YSZ meets the requirements of a NO detection electrode for the amperometric NO sensor with no or very low O_2 sensitivity and high NO sensitivity.

Conclusion

Based on the work status in the last four decades, it is concluded that the gas sensors developed so far using different techniques with different configuration could able to measure only single and binary gases. Using suitable intelligent techniques (controlling of sensitivity **and** selectivity of the sensor) and using noble materials for preparing the electrodes and electrolytes, an attempt can be made to develop a sensor which can measure minimum of four gases.

Even though it is a complex phenomena because there will be several cross reactions among the gases present in the mixture and the accumulation of gases coming out from the reactions may lead to more inaccuracy in the measured values of the gases.

Increasing the sensitivity of the sensor towards particular targeted gas species present in the mixture can be realized either by sweeping the voltage between the electrodes or by using solid electrolytes with multi-metalic electrodes. **It** is going to be **a** real challenging task for the researchers but by using step by step approach and using some intelligence algorithm this research work can be done effectively.

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