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A review of high-temperature electrochemical sensors based on stabilized zirconia

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ABSTRACT

High-temperature electrochemical sensors based on stabilized zirconia play an important role in the control of exhaust emissions and the improvement of product quality and productivity. This paper gives an overview about high temperature oxygen sensor, auxiliary electrode type sensor, and mixed potential gas sensor. The response theories of a variety of sensors are elucidated. The related measurement ranges and application examples of oxygen sensors are presented. Since air pollution regulations are being reinforced in many countries, the worldwide demand for oxygen sensors is expected to be growing. Without appropriate solid electrolyte, auxiliary electrode type sensors are developed for measuring phosphorus, sulfur, silicon, manganese and chromium in melt and CO_2, NO_x and SO_x in gas. We have described recent advances in improving the sensitivity, selectivity and long-term stability of mixed potential gas sensors which could be obtained by selecting suitable SE materials. This paper also reviews the limiting factors in measurement, the properties of stabilized zirconia and the role of electrode configuration in electrochemical sensors.

1. Introduction

It is more than a hundred years since stabilized zirconia electrolyte has been found. At present, the electrochemical sensors based on stabilized zirconia, as the most common type of sensors operating in harsh industrial environments, have been used for health and safety, energy saving, emission control in combustion processes, and industrial process control for improved product quality and productivity [1].

In order to realize the automation of production processes, improve the production efficiency and product quality, the physicochemical behavior of elements must be controlled online accurately during the smelting process. The electrochemical sensors can detect rapidly and precisely the thermodynamic activity of elements. Oxygen sensors have been widely used to control smelting process in metallurgical industry. Other elements needed to be measured include sulfur, phosphorus, silicon, manganese and chromium but no solid electrolyte exist due to the electronic conductivity and less stability. This problem can be overcome by coating the surface of stabilized ZrO_2 electrolyte with an auxiliary electrode which contains both the target element and the oxygen.

Monitoring and controlling emission of pollutants related to combustion is necessary in many industries. If gas sensors are available, they can control the combustion process and reduce the toxic emissions. The following oxygen sensors that are one of the few successful examples are discussed: equilibrium potentiometric sensors which respond logarithmically with oxygen partial pressure and amperometric sensors which need no reference gas and respond linearly with oxygen concentration. In addition to potentiometric and amperometric oxygen sensors, since mixed potential type gas sensors can measure low concentration of pollutant gases, such as NO_x, CO, hydrocarbon (HCs), H_2, and NH_3, in car exhausts or atmospheric air over the temperature range 450–900 °C, particular attention has been given during the past decades.

In this review, we discuss the principle of ZrO_2-based electrochemical sensors, the applications of oxygen sensors, the latest developments of auxiliary electrode type sensors and mixed potential type gas sensors. The limiting factors in measurement, the properties of stabilized zirconia and the role of electrode configuration in electrochemical sensors are also discussed.

2. High temperature oxygen sensors

ZrO_2-based electrochemical oxygen sensors are generally used to measure oxygen activity in gas phase and molten metal. According to

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the configuration and sensing principle, they can be classified into potentiometric and amperometric sensors.

2.1. Equilibrium potentiometric oxygen sensor

2.1.1. Response theory

When solid electrolyte is placed between different oxygen partial pressure, the electrode reactions occur at the three-phase boundary (TPB) between electrolyte, electrode, and gas [2,3].

$$O_2(g) + 4e^-(Pt) = 2O^{2-}(YSZ) \tag{1}$$

The Fermi level E_F can be controlled by the oxygen-electrode equilibrium.

$$E_F = \frac{1}{4}\left(2\mu_{O^{2-}} - \mu_{O_2}\right) \tag{2}$$

where μ is chemical potential. Assuming the chemical potential of O^{2-} remains constant within the electrolyte, the difference in Fermi levels on both sides of electrolyte is written as

$$\Delta E_F = -\frac{1}{4}\left(\mu'_{O_2} - \mu''_{O_2}\right) = -\frac{kT}{4e}\ln\frac{p'_{O_2}}{p''_{O_2}}. \tag{3}$$

The electromotive force (emf) between electrodes is expressed by the Nernst equation if the transport number of oxygen ions is unity in the electrolyte.

$$\mathrm{emf} = \frac{RT}{4F}\ln\frac{p'_{O_2}}{p''_{O_2}} \tag{4}$$

where R is the gas constant, T the absolute temperature, and F the Faraday constant. If we know the oxygen partial pressure on one side, Eq. (4) can be used to calculate the oxygen partial pressure on the other side. This is the basic principle of a potentiometric oxygen sensor. A reference air or a metal-metal oxide mixture can provide a constant oxygen activity at a given temperature.

2.1.2. Application examples

As a so-called lambda probe, it has been widely applied in automobiles, metallurgical technology and nuclear reactors.

In automobile applications the measured signal can be used directly to regulate chemical process variables and the optimal content which is of particular importance for the functioning of exhaust gas catalyzers [4]. The sensor is particularly well suited to be used near the stoichiometric point ($\lambda = 1$) where the emf signal changes sharply (Fig. 1). The λ point determines the toxic gases emissions, such as NO_x, CO and HCs. NO_x emission dominates in lean exhaust gases ($\lambda > 1$), while CO and HCs emissions prevails in rich exhaust gases ($\lambda < 1$). A three-way catalytic converter in the exhaust system can convert the exhaust gases to non-toxic carbon dioxide, nitrogen and water.

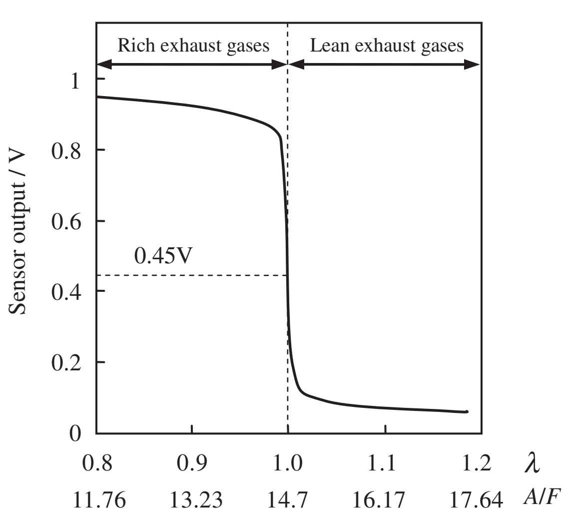

Fig. 1. Typical output signal of λ sensor.

The oxygen activity in melt, being an important process parameter in metallurgical processes, is measured by means of lambda probes. An oxygen sensor combines a thermocouple and a half-cell in a single unit (Fig. 2). If the electric leads of the reference electrode and working electrode are different materials, thermoelectric emf is generated between the two electrodes during high temperature testing. The sensor assembly should meet the following criteria [5,6]: (1) The sensor tip holding the cell and the thermocouple should be small and have a low thermal capacity; (2) It is preferable that the oxygen partial pressure in reference electrode be close to that in molten steel at 1600 °C; (3) The temperature difference between the cold junctions of thermocouple during the testing should be reduced; (4) The influence of gases released from the sensor tip should be reduced.

Millions of the oxygen sensors are consumed each year in the steel industry and copper industry. In addition to detecting oxygen, the oxygen sensors can detect other elements. It has been shown that cast iron exhibits a maximum elongation when the magnesium content is approximately 200 ppm to 750 ppm. If the activity of oxygen is obtained by oxygen sensor, the magnesium content can be calculated according to the equilibrium relationship between free oxygen and magnesium [7]. Relationship between carbon and oxygen in a large basic oxygen furnace has been established, and then the oxygen sensor can be used for determining the carbon content.

Controlling oxygen content in liquid lead-bismuth is one of the most important tasks to develop accelerator driven systems. Fig. 3 shows the relationship between emf and temperature measured in liquid lead-bismuth using oxygen sensor with yttrium-stabilized zirconia (YSZ) electrolyte and Pt/gas reference [8]. It is found that the oxygen sensor with Pt/air reference can be used to measure oxygen content in liquid lead-bismuth above 450 °C.

2.2. Amperometric (limiting current) oxygen sensor

To improve fuel economy, gasoline direct-injection engines and lean burn engines were developed [9–11]. However, the Nernst measuring principle with insufficient lambda-range is difficult to be applied to fuel lean conditions. For lean burn applications, it has to be replaced, e.g. by an amperometric principle [9,12,13].

2.2.1. Response theory

By applying a voltage to the solid electrolyte, oxygen is electrochemically transferred through the electrolyte from the cathode to the anode. When the voltage is high enough to make O_2 at the cathode be close to zero, the current saturates at a value depending on the measured oxygen concentration. The limiting current sensing mechanism is well known for detecting dissolved oxygen in liquids. However, since the

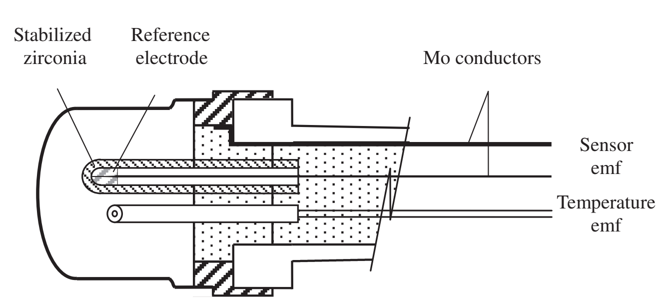

Fig. 2. Schematic diagram of sensor for measuring oxygen in molten steel.