

# Measurement and control of oxygen partial pressure at elevated temperatures

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## ARTICLE INFO

### Article history:

Received 13 July 2012

Received in revised form 15 February 2013

Accepted 28 February 2013

Available online 14 March 2013

### Keywords:

Potentiometric sensor

Oxygen ion pump

Electromagnetic levitation

Yttrium-stabilized zirconia

## ABSTRACT

In order to measure and control of the oxygen partial pressure at elevated temperatures in the range from  $10^{-20}$  to  $10^{-3}$  bar a standalone system is developed. One major component of the system is a potentiometric sensor which exhibits a measurement uncertainty of  $\Delta \log(p_{O_2} / \text{bar}) < 0.02$ . The adjustment of the oxygen partial pressure is realized using an oxygen ion pump. Here, a pulse-width modulated electric current between  $-10$  and  $+10$  mA is applied to yttrium-stabilized zirconia resulting in oxygen transport into or out of the system. The pump shows an accuracy in oxygen flow of  $10^{-9}$  l/min and enables, therefore, the adjustment of  $p_{O_2}$  with an uncertainty of  $\Delta \log(p_{O_2} / \text{bar}) < 0.02$  even in buffers like CO/CO<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>O close to the stoichiometric composition. Further, the impact of different temperatures at the positions of sensor and sample on the oxygen partial pressure is discussed. Finally, the application of the system in an electromagnetic levitator is presented. Here, a Ni sample is heated to 1720 °C and the surface tension of the melt is determined as a function of oxygen partial pressure.

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## 1. Introduction

In order to investigate materials parameters at elevated temperatures, precise knowledge about the oxygen partial pressure,  $p_{O_2}$ , and the ability to control it, are required in many cases. One example is the determination of surface tension and viscosity of molten samples using electromagnetic levitation [1]. Using this method, the sample is levitated in an electromagnetic field. The eddy currents induced in the sample are used to heat it up to a certain temperature [2]. As soon the sample is molten, the materials parameters, such as the surface tension and/or viscosity, are determined from free oscillations of the levitating liquid sphere. The movement of the sample surface is commonly recorded using a high-speed CMOS camera [3]. Such systems enable contactless analysis of materials and are, therefore, suitable for investigation of e.g. high-purity metals and reactive materials. The approach is suited for materials with relatively high electric conductivity. Nevertheless, it is possible to analyze semiconductors such as silicon [4]. Here, the levitation force induced from the electromagnetic field is smaller by over three orders of magnitude than in case of metals. Nevertheless, the eddy current is sufficiently high to heat the sample. Since the electric conductivity of semiconductors increases with temperature, the force also increases and the sample starts to levitate. Molten silicon exhibits metallic behavior and can be investigated using the levitation technique.

Even though electromagnetic levitation guarantees no contamination from crucible, oxide films or dissolved oxygen may lead to significant change of materials properties, such as surface tension or viscosity. Therefore, the ability to control and measure  $p_{O_2}$  during the entire experiment is mandatory. The  $p_{O_2}$  control is also required for the investigation of novel high-temperature materials for e.g. gas sensors, where precise knowledge of transport phenomena or oxygen diffusion defines the potential application limits [5].

Conventional optical or photoacoustic oxygen sensors are hardly applicable for such high-temperature experiments. Here, the accessible  $p_{O_2}$  range is too narrow. Beyond that, those sensors provide commonly the total oxygen content, which does not necessarily correspond to the property of interest, i.e. the oxygen activity. Here, a solid-state gas sensor operated at the same temperature as the sample is the best solution since sample and sensor experience the same oxygen activity. Among solid-state devices, the potentiometric sensor appears to be most favorable due to its short response time and wide range of measurable  $p_{O_2}$ .

Conventional gas mixing systems are not able to control the oxygen partial pressure within the entire  $p_{O_2}$  range of interest from  $10^{-24}$  to  $10^0$  bar due to mechanical constraints. Above  $10^{-7}$  bar, the  $p_{O_2}$  can be adjusted by mixing inert gases with oxygen using cascades of mass flow controllers. When  $p_{O_2}$ 's below  $10^{-15}$  bar are required, buffer gases, like CO/CO<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>O can be used. Here, the reaction between oxygen and, for example, hydrogen may be slightly shifted using mass flow controllers thereby enabling adjustment of the  $p_{O_2}$  with satisfactory accuracy. Mechanical mass flow controllers, which show commonly a resolution of about  $50 \text{ mm}^3/\text{min}$  are, however, too inaccurate to adjust the  $p_{O_2}$  in

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the intermediate range close to the equilibration point of buffer mixtures. Here, very little changes in gas composition shift the equilibrium of the buffer gas reaction with oxygen drastically, resulting in  $p_{O_2}$  changes of several orders of magnitude. Nevertheless, the  $p_{O_2}$  in this range may be controlled using an oxygen ion pump. Their oxygen flow resolution is commonly better than  $0.001 \text{ mm}^3/\text{min}$ .

The scope of the paper is to present the operation principle of a newly developed oxygen loading system (OLS) in concert with a specific application which is the determination of the  $p_{O_2}$  dependent surface tension of molten metals using an electromagnetic levitator. Thereby, the influence of buffer gases like  $\text{CO}/\text{CO}_2$  or  $\text{H}_2/\text{H}_2\text{O}$  on the  $p_{O_2}$  and the temperature dependent equilibrium of buffer gas mixtures are discussed. Further, the performance of the OLS and an exemplarily result for the surface tension of molten Ni are given.

## 2. Measurement and control of the oxygen partial pressure

### 2.1. Potentiometric sensor

A potentiometric sensor determines the difference of the oxygen activity in two gas compartments separated by an electrolyte. The latter is, in most cases, a solid-state ionic conductor such as  $\text{Y}_2\text{O}_3$ -stabilized zirconia (YSZ). Yttrium doping increases the stability at elevated temperatures and increases the concentration of oxygen vacancies and thus, the ionic conductivity of the material [6,7]. The activity of gaseous components corresponds nearly to their partial pressures, which will be used for the further discussion. The electromotive force of such electrochemical cells depends on the temperature  $T$  and can be expressed by the Nernst equation

$$E_{\text{cell}} = \frac{RT}{4F} \ln \left( \frac{p_{O_2}}{p_{O_2}^{\text{ref}}} \right), \quad (1)$$

where  $R$  and  $F$  correspond to the universal gas constant and the Faraday constant, respectively. The properties  $p_{O_2}$  and  $p_{O_2}^{\text{ref}}$  denote the oxygen partial pressure in the gas of interest and in the reference gas, respectively. The electromotive force has to be measured with high-input impedance instruments.

The most remarkable feature of potentiometric sensors is their operation without calibration. The electromotive force of such devices depends solely on the  $p_{O_2}$  on both sides of the electrolyte and its temperature. Therefore, it is sufficient to provide a well-known reference gas and to control (or measure) the temperature of the electrolyte precisely. The potentiometric sensor shows a very good long-term stability and sensitivity. The change in voltage for the variation of  $p_{O_2}$  by one order of magnitude does not depend on the  $p_{O_2}$  range. Hence, the sensor ensures accuracy independent on the absolute  $p_{O_2}$ . The solid-state electrolyte enables reliable operation down to a  $p_{O_2}$  of about  $10^{-30}$  bar.

The potentiometric sensor has to be operated at a temperature, which is high enough to enable sufficient ionic conductivity. Doped zirconia fulfills this condition above about  $500^\circ\text{C}$ . Electronic contributions become relevant at very high temperatures and low  $p_{O_2}$ 's. They lower the electromotive force due to internal shortening [8]. For example, at  $800^\circ\text{C}$  the condition  $\sigma_e \leq 0.1 \sigma_{\text{ionic}}$  is fulfilled for  $p_{O_2}$ 's above about  $10^{-35}$  bar. At  $1000^\circ\text{C}$ , the electronic conductivity is lower than the ionic conductivity by at least one order of magnitude for  $p_{O_2}$ 's above  $10^{-30}$  bar [8]. Those values are commonly far below the experimentally adjustable  $p_{O_2}$ . Considering the dominance of the ionic conductivity and long-term stability, operation temperatures between  $600$  and  $800^\circ\text{C}$  are regarded to be most suited. In this temperature range a typical response time of  $10$ – $100$  ms is achieved [9].

### 2.2. Oxygen ion pump

The operation principle of the oxygen ion pump is reversed with respect to the potentiometric sensor described above. Here, an electric current is applied to the electrodes and the charge is moved across the electrolyte in form of oxygen ions. At the negative electrode oxygen is incorporated into oxygen vacancies of the electrolyte,  $V_{\text{O}}^{\circ\circ}$ , while at the positive electrode oxygen leaves the crystal lattice and forms gaseous oxygen. In case of dominant ionic conductivity, the flow of oxygen ions,  $J_{O_2}$ , is related to the electric current  $I$  by

$$J_{O_2} = \frac{I}{4F} \quad (2)$$

where  $F$  corresponds to Faraday constant [10].

The pump consists of the same solid-state electrolyte as the potentiometric sensor described above. The schematic drawing of the pump is shown in Fig. 1. Again, the operating temperature must be sufficiently high to promote the transport of  $\text{O}^{2-}$  through the electrolyte, but low enough to suppress the electronic conduction and to minimize the long-term degradation of the pump.

Assuming that the oxygen flow does not alter the total pressure significantly, the oxygen partial pressure at the output of the pump depends on the electric current, total pressure  $p_{\text{tot}}$  and the initial oxygen partial pressure in the carrier gas  $p_{O_2}^0$ :

$$p_{O_2} = p_{O_2}^0 + p_{\text{tot}} \frac{J_{O_2}}{J_{\text{tot}}} \quad (3)$$

The oxygen partial pressure is measured using an additional potentiometric sensor (see Fig. 1) at the output of the oxygen ion pump. Here, a PID controlled feedback loop adjusts the pumping current so that the desired  $p_{O_2}$  at the additional sensor is maintained.

For the reference  $p_{O_2}^{\text{ref}} = 0.209$  bar (ambient air) is assumed. The error introduced by this simplification is negligible. During operation of the oxygen ion pump special attention has to be paid on the current source. Here, the potential applied to the electrodes must not exceed the decomposition voltage of about  $2$  V.

### 2.3. Oxygen partial pressure in buffer gas mixtures

In case of the presence of buffer gas mixtures such as  $\text{CO}/\text{CO}_2$  or  $\text{H}_2/\text{H}_2\text{O}$  the equilibrium of oxygen with these components has to be taken into account. Here the  $p_{O_2}$  at the output of the oxygen ion pump as described by Eq. (3) does not apply. In case of hydrogen containing atmospheres, oxygen reacts with hydrogen and forms water vapor according to

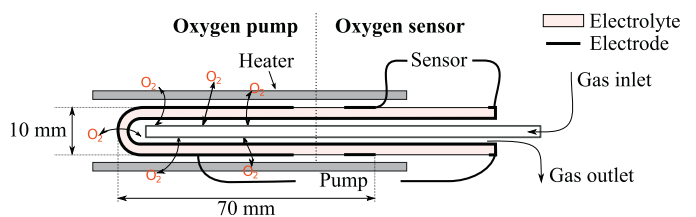


Fig. 1. Schematic drawing of an YSZ oxygen ion pump consisting essentially of an electrolyte (YSZ), electrodes (Pt), a gas inlet (alumina) and a heater. The carrier gas is delivered to the pumping area, where oxygen is transferred across the solid-state electrolyte at a temperature of  $600^\circ\text{C}$ . The resulting  $p_{O_2}$  is measured in the sensor area using an additional electrode on the same YSZ tube.

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