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Quantitative Model of the Behavior of the Limiting Current Oxygen Sensors

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Abstract

A physicochemical model of the I(V) response of amperometric oxygen sensors based in ion conduction is proposed. Although the qualitative behavior of these devices is well known, there is a lack of a quantitative description of the response of the sensors in their normal operation conditions. The model focuses on diffusion across a porous layer and minimization of the oxygen-ion electrochemical potential in steady state. It provides an analytical expression describing the current-voltage dependence in terms of oxygen diffusivity, ionic conductivity, temperature and geometrical parameters. Experimental measurements of our own-designed amperometric ceramic sensors are in agreement with the proposed model.

Keywords: oxygen sensor; limiting current; YSZ; amperometric

1. Introduction

Oxygen sensors have been developed for automotive or environmental applications in the last decades. Different working principles have been proposed for oxygen sensors: catalytic, optical, resistive, electrochemical sensors have been designed. In the context of electrochemical sensors, one of the existing devices is the amperometric sensor, also known as limiting current sensor. It generates a current which is proportional to the molecular oxygen partial pressure in the measured gas. The aim of this work is to present a physicochemical model of the current-voltage characteristics of the amperometric oxygen sensor and to fit the model to experimental data from our own-designed sensors.

1.1 Qualitative description

Fig 1 shows the basic structure of a limiting current oxygen sensor and its normal operation mode.

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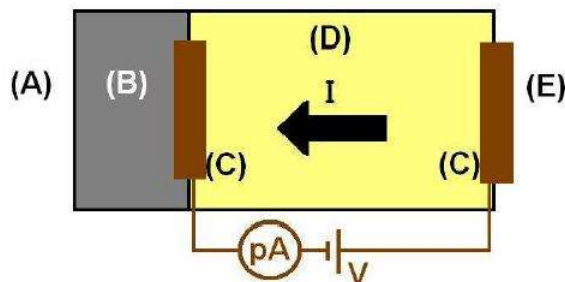


Fig.1. Schematic cross-section view of an amperometric sensor and operation mode. (A) Measured gas, (B) Diffusive layer, (C) Electrodes, (D) Ion-conducting electrolyte, (E) Reference gas. The external voltage V is applied and a certain net current I is detected. In the limiting current region, this current is linear to the concentration of oxygen in the measured gas.

The sensing element consists in a ceramic electrolyte (D), usually made of yttria-stabilized zirconia (YSZ) or any other ceramic with O^{2-} ion-conducting properties¹. This electrolyte is covered by two metallic or ceramic-metallic catalytic electrodes (C), exposed to two gaseous atmospheres. These atmospheres can be the measured gas (A) and an air reference (E) or just the same measured gas in the two electrodes. The working electrode is protected by the diffusive layer (B), made of a porous material such as spinel or YSZ. Gas molecules diffuse across this layer before reaching the measuring electrode. When an external voltage is applied, the system is pushed to a non-equilibrium state and a net flow of oxygen ions is generated as there is a gradient of energy across the device due to differences between electrical potential and chemical potential of oxygen ions in each point of the electrolyte. Gas molecules from the measured gas diffusing across the protective layer may react at the three phase boundary sites in the interfaces between the electrode and the electrolyte following the well-known reaction,



In this equation O_2 molecules come from the measured gas and electrons are provided by the metal catalyst. O^{2-} ions are subsequently provided to, or extracted from, the electrolyte according to the magnitude of the applied voltage. When the applied voltage is low, the current is linear with the voltage as depicted in Fig 2. However, if the polarization is high, the current may be saturated, as the charge exchange rate demanded by the external voltage may be too high in comparison to the rate of oxygen diffusion across the porous layer. The flow of oxygen molecules diffusing across the layer is linked to the O_2 partial pressure in the gas. It can be shown² that the relation between the limiting current and the O_2 concentration is:

$$I(V = +\infty) = 4eS \frac{D}{L} n_{GAS} \quad (2)$$

where e is the elementary charge, D is the oxygen effective diffusion coefficient in the porous layer, S is the electrolyte section, L is the layer's width and n_{MEAS} is the O_2 concentration in the measured gas.

2. Experimental

Some amperometric sensors were designed with monolithic ceramic technologies³, fired at 1450C for 30 minutes and measured in a gas testing station in order to reproduce the well-known qualitative behavior of these devices and try to fit a physicochemical model of their response. Four different series of sensors were designed, as shown in Table 1. All sensors incorporated electrodes made of Pt and YSZ to contain a large density of three phase boundary sites. A heating resistance of 9Ω was put together with the sensing device and polarized at 13V to reach a high enough temperature, around 600°C. The only difference between the four series of sensors was the porosity of their layers (high in the case of the layer made of YSZ:graphite 4:1 and very low in the YSZ:carbon nanofibers 20:1) and the ionic conductivity due to the different content of Y_2O_3 in the ZrO_2 matrix (4.5Y or 5Y). These differences were incorporated to see how different the current-voltage characteristics of the four series of sensors were in terms of those physical properties.

Table 1. Designed sensors, with their differences in yttria content in the electrolyte and porosity in the diffusive layer.

Sensor type	Electrolyte	Diffusive layer
A	ZrO ₂ with 4.5% wt of Y ₂ O ₃ (YSZ 4.5Y)	YSZ mixed with graphite in a proportion of 4 to 1
B	ZrO ₂ with 4.5% wt of Y ₂ O ₃ (YSZ 4.5Y)	YSZ mixed with carbon nanofibers in a proportion of 20 to 1
C	ZrO ₂ with 5% wt of Y ₂ O ₃ (YSZ 5Y)	YSZ mixed with graphite in a proportion of 4 to 1
D	ZrO ₂ with 5% wt of Y ₂ O ₃ (YSZ 5Y)	YSZ mixed with carbon nanofibers in a proportion of 20 to 1

All sensors incorporated electrodes made of Pt and YSZ to contain a large density of three phase boundary sites. A heating resistance of 9 Ω was put together with the sensing device and polarized at 13V to reach a high enough temperature, around 600°C. The only difference between the four series of sensors was the porosity of their layers (high in the case of the layer made of YSZ:graphite 4:1 and very low in the YSZ:carbon nanofibers 20:1) and the ionic conductivity due to the different content of Y₂O₃ in the ZrO₂ matrix (4.5Y or 5Y). These modifications were incorporated to see how different the current-voltage characteristics of the four series of sensors were in terms of those different physical properties. SEM images of the two different layers can be seen at Fig 3 (a) and (b). Impedance spectroscopy was carried out to detect the polarization resistance of the sensors.

3. Results and discussion

The sensors were exposed to several mixtures of molecular oxygen dissolved in nitrogen. As an example, the *I-V* characteristics for the four different sensors exposed to 2% and 6% O₂ concentration at 600°C are shown in Fig 3.

Several hypothesis were taken into account in the proposed model. Only ionic conduction was considered, with no electron contribution. Also, only steady state conditions were examined. The Gibbs free energy in each point of the electrolyte was assumed to be equivalent to the electrochemical potential μ^* , which is the superposition of the chemical potential and the electric energy.

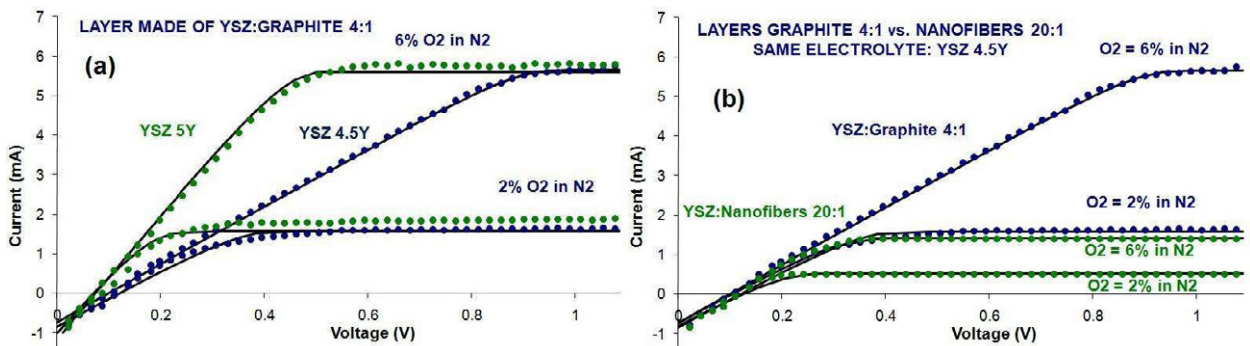


Fig.2. Experimental measurements with the four series of sensors and model fit. Fitted parameters: ionic conductivity and oxygen diffusivity in the layer. (a) Sensors A and C, i.e. same layer (the porous one) but different electrolyte, 4.5Y and 5Y respectively. (b) Sensors B and D, i.e. same electrolyte YSZ 4.5Y but different layer (dense and porous).

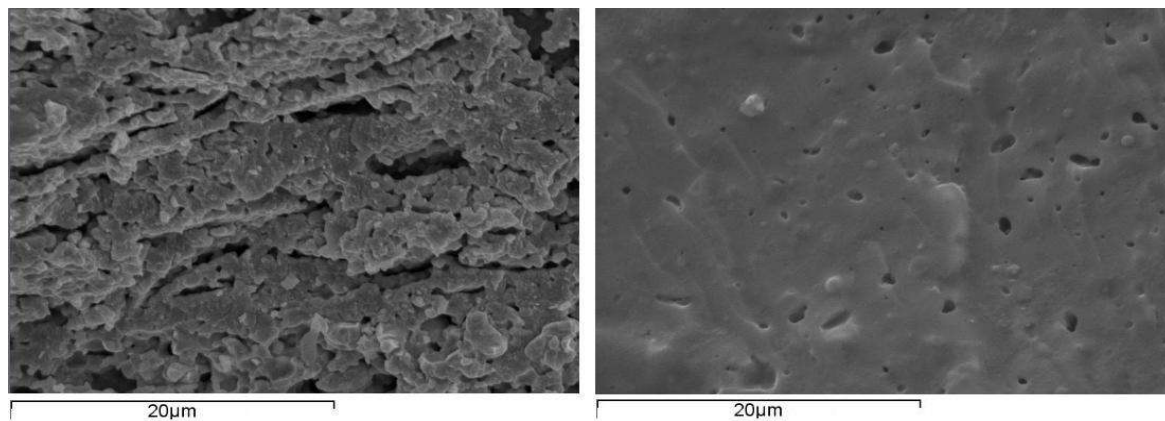


Fig.3. SEM images of the two different protective layers. The left one is made of YSZ mixed with graphite in a proportion of 4 to 1. The right one is made of YSZ mixed with carbon nanofibers in a proportion of 20 to 1. As expected, the YSZ:graphite 4:1 layer shows a higher porosity than the YSZ:nanofibers 20:1, which appears to be extremely dense. As a consequence, a higher diffusivity is obtained in sensors A and C, and subsequently higher limiting currents are detected for these sensors, with no influence on the linear regime.

Fick's law of diffusion in the porous layer for oxygen molecules was considered in the porous layer. A linear relation between the flow of oxygen ions in the ceramic electrolyte and the gradient of electrochemical potential between the two electrodes was considered. In analogy to the transport theory of electrons, the ionic conductivity was found to be this linear coefficient linking the two magnitudes. By applying mass conservation for oxygen molecules in the layer and oxygen ions in the electrolyte and after a bit of algebra⁴, a transcendent equation $I(V,I)$ for the current-voltage characteristics was extracted:

$$I = \frac{1}{R} \left(V - \frac{k_B T}{4e} \ln \frac{n_{REF}}{n_{GAS} - \frac{I \times L}{4eSD}} \right) \quad (3)$$

In this equation, R is the polarization resistance, n_{REF} is the oxygen concentration in the reference, T is the temperature and k_B is Boltzmann's constant. For very high voltage it recovers the original expression (2) for the limiting current. By fitting the values of polarization resistance and oxygen diffusivity in the layer (Fig.2), the different behaviors of the different sensors A, B, C and D were correctly described. It was confirmed that the limiting current is influenced by the diffusivity whereas the linear regime is influenced mainly by the ionic conductivity of the electrolyte.

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