

Response behaviour of oxygen sensing solid electrolytes

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The response time (t_r) after a step change in oxygen partial pressure was investigated for some solid electrolytes used in Nernst type oxygen sensors. The electrolyte as well as the (porous) electrode material affect the value of t_r . Stabilized Bi_2O_3 materials exhibit slower response rates (larger t_r values) than stabilized ZrO_2 . Introduction of Bi_2O_3 in stabilized ZrO_2 increases the response time.

Gold electrodes show a higher response rate than platinum in the oxygen partial pressure and temperature region used.

1. Introduction

Solid electrolytes which exhibit oxygen ion conductivity at intermediate temperatures are suitable for use in oxygen sensors. In most cases stabilized ZrO_2 is used [1] in combination with noble metal electrodes. A potential difference (E) between the electrodes of the sensor is developed when different oxygen partial pressures P'_{O_2} and P''_{O_2} exist on each side of the sensor. According to Nernst the following relation holds:

$$E = \frac{RT}{nF} \ln (P'_{\text{O}_2}/P''_{\text{O}_2}) \quad (1)$$

The response time is defined as the time lag between a step change in bulk oxygen partial pressure and the final value of E registered by the sensor. Little attention is paid in the literature to quantitative measurement and analysis of the response time, t_r , of oxygen sensors. This may be due to the fact that oxygen sensors are frequently used at high temperatures. At these temperatures ($\geq 700^\circ\text{C}$) an electrochemical response time of a few milliseconds is calculated for stabilized ZrO_2 [2]. In practical sensors the ultimate value of t_r is larger and is governed by aerodynamic conditions and diffusion limitations.

Long-term e.m.f. changes were investigated at high temperatures [3, 4]. These changes may arise because of different transport properties of

impurity phases which have a lower oxygen transport number than the main phase. The rate limiting chemical diffusion process within the bulk of the electrolyte is many orders of magnitude slower than the equilibratory reaction at the electrode-electrolyte surface after a P_{O_2} step change. This long-term process results in a final potential change of a few per cent of the e.m.f. difference measured immediately after the P_{O_2} change [4] and can be seen as a secondary effect.

Anderson and Graves [5] have performed experiments on ZrO_2 tubes with platinum paste electrodes and gas flow rates of $16\text{--}32\text{ cm}^3\text{ s}^{-1}$. Here the diffusive mass transport from the bulk gas to the reaction sites at the sensor surface is rate determining. If higher gas flow rates and porous electrodes are used other processes can be studied such as the reactions at the electrode-electrolyte-gas interface. The electrodes of the sensor are often covered by a gas permeable membrane in order to prevent contamination of the electrodes. In this case the response time is also governed by the diffusion rate of the oxygen from the bulk gas to the electrode [6].

The materials used in this investigation were pure and Bi_2O_3 -doped stabilized ZrO_2 and stabilized Bi_2O_3 . Well-defined and porous platinum or gold electrodes were used. In this way we compared stabilized ZrO_2 used in commercial sensors with Bi_2O_3 based materials which exhibit a higher

ionic conductivity [7] and a lower electrode resistance [8]. Furthermore the effect of the modification of yttria-stabilized zirconia with Bi_2O_3 was studied.

2. Experimental method

Yttrium stabilized ZrO_2 (ZY) and erbium stabilized Bi_2O_3 (BE) were investigated. The composition of the electrolyte materials is given in Table 1. The ZYB samples are Bi_2O_3 -doped ZrO_2 - Y_2O_3 materials (ZY17 or ZY21). The ZYB1 sample is obtained from pure ZY17 treated for 2 h in a Bi_2O_3 atmosphere. The other ZYB samples contain a certain percentage of Bi_2O_3 in the bulk phase. The ZYB2 is a monophasic Bi_2O_3 doped specimen which does not contain any monoclinic ZrO_2 [9]. The Bi_2O_3 is stabilized with different amounts of Er_2O_3 (BE samples in Table 1). After isostatic pressing and sintering all samples exhibit a theoretical density of 95% or more. The electrolytes used for response measurements have a diameter of about 10 mm and a thickness of 1–2 mm. The electrodes were sputtered on the polished electrolyte surfaces. The method has been published elsewhere [8] and results in well-defined porous electrodes.

The sensors obtained in this way were used for the response time measurements performed in the cell which is schematically given in Fig. 1. The sensor (1) is placed on an Al_2O_3 ring (3). This ring, with a Pt paste electrode on the top, is placed in a

Table 1. Composition of the investigated materials

Sample number	Composition (mol %)			
	ZrO_2	$\text{YO}_{1.5}$	$\text{BiO}_{1.5}$	$\text{ErO}_{1.5}$
ZY17	83	17	–	–
ZY21	79	21	–	–
ZYB1	83	17	?*	–
ZYB2	78	20.6	1.4	–
ZYB3 [†]	78.3	20.7	1	–
ZYB4 [†]	79.5	16.3	4.2	–
BE20	–	–	80	20
BE30	–	–	70	30
BE40	–	–	60	40

* Sample ZYB1 is ZY17 treated in Bi_2O_3 atmosphere (see text).

[†] These samples contain a fraction of a monoclinic ZrO_2 -phase.

stainless steel cylinder. Another Al_2O_3 ring with a platinum contact (2) is placed on the sensor. The upper gas supply tube (4) and the weight (6) attached to it provide an airtight seal between sensor and ring (3). Sensor and upper ring (2) are surrounded by an Al_2O_3 -cylinder (7) in order to retain sensor and supply tube (4) in the correct position. An air stream continuously flows through the upper supply tube ($2 \text{ cm}^3 \text{ s}^{-1}$). The gas stream through the lower tube can be switched from air to oxygen and reversely by means of two electrically driven magnetic valves (9). The switching time between these valves is 15 ms. The cell is placed in a tube furnace (10). The sensor voltage as function of time is registered by a Biomation 805 waveform recorder having a maximum sampling speed of one measurement per 10^{-3} s . The voltage signal is followed by an oscilloscope and afterwards indicated on a chart recorder.

3. Results and discussion

In Fig. 2 typical response curves are given after step changes from low to high P_{O_2} ($0.21 \rightarrow 1 \text{ atm}$) and from high to low P_{O_2} ($1 \rightarrow 0.21 \text{ atm}$). The sensor voltage as a function of time (t) after a step change in P_{O_2} , $V(t)$, can be described by the empirical relation given by [10]:

$$V(t) - V(0) = [V(\infty) - V(0)] \exp(-t/\tau)^{1/2} \quad (2)$$

$V(t)$, $V(0)$ and $V(\infty)$ are sensor voltages at $t = t$, $t = 0$ and $t = \infty$, respectively. τ is a characteristic time parameter which follows an Arrhenius-type law [10]:

$$\tau = A(P_{\text{m}})^{-1/2} \exp(E_{\text{act}}/RT) \quad (3)$$

A is a constant and P_{m} is the mean oxygen partial pressure, $P_{\text{m}} = [P(\text{initial}) + P(\text{final})]/2$. In our experiments P_{m} is constant so a new constant $\tau_0 = A(P_{\text{m}})^{-1/2}$, can be introduced in Equation 3. A combination of Equations 2 and 3 gives:

$$t = \tau_0 \ln^2 \left[1 - \frac{V(t) - V(0)}{V(\infty) - V(0)} \right] \exp(E_{\text{act}}/RT) \quad (4)$$

In Fig. 3 Equation 4 is fitted for the response data in Fig. 2. It can be seen from Fig. 3 that Equation 4 is in good agreement with our results when $t > 0.5 \text{ s}$. The time below which Equation 2

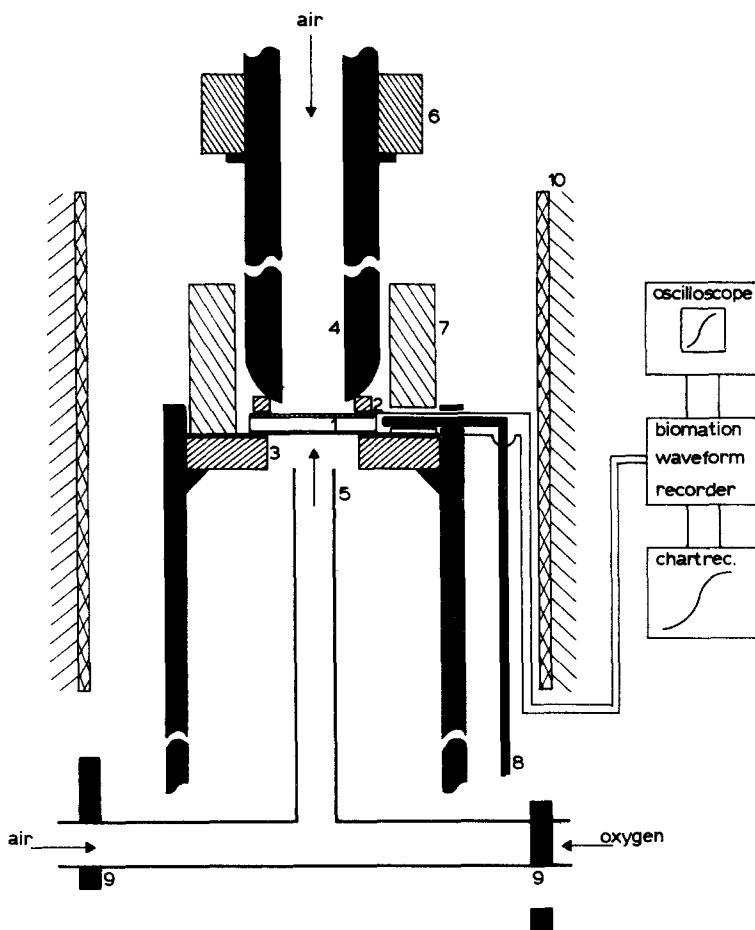


Fig. 1. Cell used in response measurements: 1. sensor, 2. and 3. Al₂O₃ rings with platinum contacts, 4. and 5. gas supply tubes, 6. weight, 7. Al₂O₃ cylinder, 8. thermocouple (Pt-Pt 10% Rh), 9. electrically driven magnetic gas valves, 10. tube furnace wall.

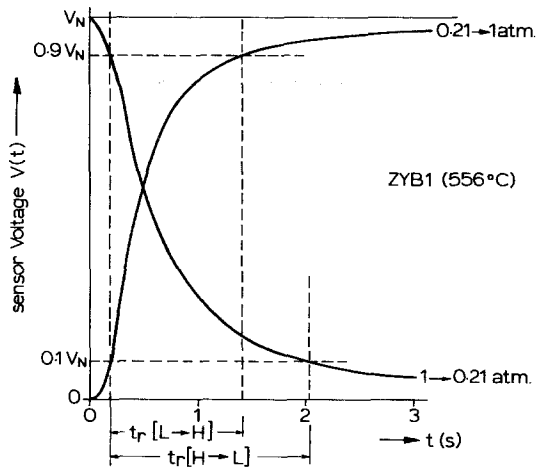


Fig. 2. Response curves after P_{O_2} change from 0.21 to 1 atm and reverse. V_N = Nernst potential.

does not hold (0.5 s) is independent of temperature. When $t < 0.5$ s, $V(t) - V(0)$ is proportional to $\exp(-t/\tau)$. This relation and the independence of the temperature suggests a diffusion and a mixing process of oxygen and air as the rate determining step for $t < 0.5$ s.

The response time (t_r) used in this work is defined as:

$$t_r = t_{0.9} - t_{0.1} \quad (5)$$

where $t_{0.9}$ and $t_{0.1}$ are the times at which $V(t) = 0.9 V(\infty)$ and $V(t) = 0.1 V(\infty)$, respectively. The starting point of the measurement is chosen as the time at which $V(t) = 0.1 V(\infty)$ because the time delay between P_{O_2} switch and transport to the sensor is difficult to calculate accurately from the experimental curves. It can be seen from

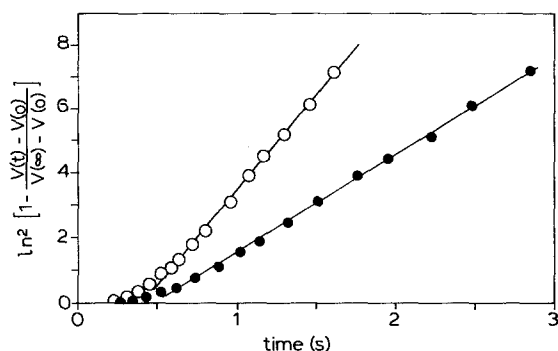


Fig. 3. Voltage variation after P_{O_2} step change. Open points: 0.21 \rightarrow 1 atm; closed points 1 \rightarrow 0.21 atm.

Equations 4 and 5 that the time needed to reach the point 0.1 $V(\infty)$ is less than 0.5% of the total response time (t_r). Equation 4 shows that the choice of the time at which $V(t) = 0.9 V(\infty)$ does not affect the value of E_{act} .

It can be seen from Fig. 2 that the value of t_r after a step change from low to high P_{O_2} is smaller than the t_r value after a P_{O_2} step change in the reverse direction ($t_r[L \rightarrow H] < t_r[H \rightarrow L]$).

Anderson and Graves [5] and Fouletier *et al.* [10] found the same type of dependence of t_r on the direction of the oxygen concentration change. Anderson and Graves [5] used normalized functions, $\phi_V(t)$ and $\phi_c(t)$, defined by:

$$\phi_V(t) = \frac{|V(t) - V(\infty)|}{|V(0) - V(\infty)|} \quad (6)$$

$$\phi_c(t) = \frac{|P_{O_2}(t) - P_{O_2}(\infty)|}{|P_{O_2}(0) - P_{O_2}(\infty)|} \quad (7)$$

Oxygen pressures $P_{O_2}(t)$ at time t used in Equation 7 are derived from experimental $V(t)$ values with the help of Equation 1. In this work an oxygen concentration change from low to high values gave slightly different $\phi_V(t)$ as well as $\phi_c(t)$ values if these are compared with a concentration change in the reverse direction. Anderson and Graves [5] found $\phi_c(t)$ values independent of the direction of the P_{O_2} changes. According to them [5] this similarity in $\phi_c(t)$ values indicates a diffusive mass transport to or from the electrolyte surface as a rate determining step. The difference in $\phi_c(t)$ values observed for a sensor at a fixed temperature suggests that other processes at the gas-electrode-electrolyte interface play a role in the

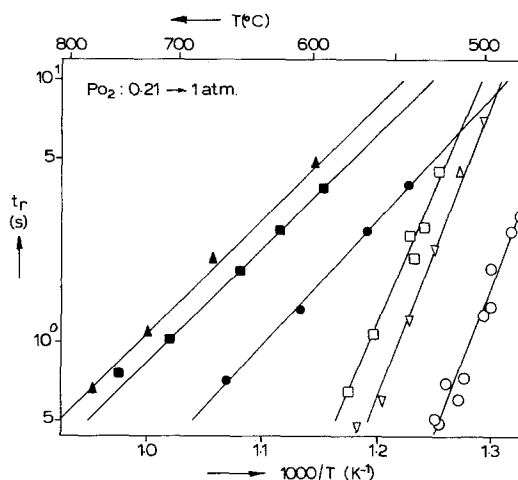


Fig. 4. Response time as a function of temperature for stabilized ZrO_2 and stabilized Bi_2O_3 . ∇ - ZY17; \square - ZY21; \circ - ZY21 (gold electrode); \bullet - BE20; \blacksquare - BE30; \blacktriangle - BE40.

response behaviour. This suggestion is supported by the fact that we use porous, thin electrodes (sputtered instead of paste); a factor which eliminates diffusion limitations.

Response times as function of temperature are given in Figs. 4 and 5. It can be seen that the electrolyte material as well as the electrode material influence the response time. The activation energies (E_{act}) are calculated from the Arrhenius plots and are given in Table 2. In this table the temperatures are also given at which t_r is 1 s and

Table 2. Response data after a P_{O_2} step change from 0.21 to 1 atm

Sample number**	E_{act} ($kJ\ mol^{-1}$)	T_1 ($^{\circ}C$)*	T_{10} ($^{\circ}C$)*
ZY17	208	565	490
ZY21	199	585	501
ZY21 (Au)	216	524	457
ZYB1	156	591	487
ZYB2	130	638	504
ZYB3	169	633	529
ZYB3 (Au)	159	614	505
ZYB4	205	634	550
BE20	91	688	487
BE30	84	780	527
BE40	82	808	543

* T_1 and T_{10} are temperatures at which t_r is 1 and 10 s, respectively.

** If not mentioned Pt electrodes were used.

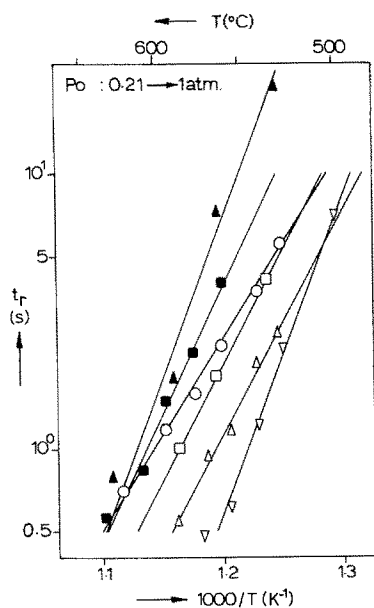


Fig. 5. Response time as a function of temperature for pure and Bi_2O_3 doped $\text{ZrO}_2\text{-Y}_2\text{O}_3$. ∇ - ZY17; \triangle - ZYB1; \circ - ZYB2; \blacksquare - ZYB3; \blacktriangle - ZYB4; \square - ZYB3 (gold electrode).

10 s (T_1 and T_{10} , respectively). These data enable us to compare the different sensors.

3.1. Response behaviour of stabilized ZrO_2 and Bi_2O_3 with Pt electrodes

The response data for these materials are given in Fig. 4 and Table 2. It can be seen from these results that sensors based on stabilized ZrO_2 have a smaller response time compared with stabilized Bi_2O_3 in the observed temperature region. At temperatures lower than 500°C bismuth oxide materials may be advantageous (see Fig. 4).

The (electrochemical) response time is influenced by at least two factors. First a charge transfer of electrons takes place from the electrode and from the electrolyte to the adsorbed oxygen species (or in the reverse). This results in the formation of a charged (double) layer in the electrolyte region which is directly associated with the electrodes. This region is called the electrode zone with the Debye-Hückel length L_D as characteristic thickness [11]:

$$L_D = \left(\frac{\epsilon k T}{8 \pi n_i e_0^2} \right)^{1/2} \quad (8)$$

where ϵ is the relative dielectric constant, and n_i the number of univalent particles per cm^3 with positive or negative excess charge in the lattice. The value of L_D can be rather large in these types of material.

In the process described above the *rate* of oxygen adsorption and the formation *rate* of the charged layer determines the response time after a P_{O_2} step change. It is suggested in the literature that bismuth sites are active places with regard to oxygen adsorption. This was found in solid electrolytes [8, 12] and catalysts such as BiOBr [13]. Therefore in materials having these sites an extra adsorption surface for oxygen is present.

The double layer formation in the electrode zone results in a reorganization in defect structure in this zone without a net change in stoichiometry. The rate of this reorganization can be correlated with the conductivity of the electrode zone. The BE 40 specimen has a lower conductivity than BE 30 while BE 20 has the highest conductivity [7]. Hence within the group of stabilized Bi_2O_3 the decrease in response time may be due to a decreasing electrolyte resistance.

The difference in response behaviour between stabilized Bi_2O_3 and ZrO_2 can be determined by a second process. This will be discussed below.

The second factor which influences the response time is the *amount* of oxygen species necessary to attain the Nernst e.m.f. Here a change in stoichiometry takes place in the electrode zone by means of redox reactions. This process can be associated with the electrical low frequency capacity (C_{LF}) which has the character of a pseudo capacitance. Higher C_{LF} values result in more oxygen species in the electrode zone which are necessary to attain the final Nernst e.m.f. High C_{LF} values were found for Bi_2O_3 specimens [14]. The BE samples have a higher double-layer capacity (C_{DL}) than ZY [8]. The high C_{DL} ($> 10 \text{ F m}^{-2}$) for BE suggests that no pure C_{DL} is measured but that a part of it also plays a role in the C_{LF} process. This C_{LF} may result in larger response times of stabilized Bi_2O_3 compared with stabilized ZrO_2 in the observed region.

3.2. Response behaviour of pure and Bi_2O_3 doped $\text{ZrO}_2\text{-Y}_2\text{O}_3$ with Pt electrodes

It can be seen from Fig. 5 and Table 2 that t_r

increases at a fixed temperature when Bi_2O_3 is introduced into $\text{ZrO}_2\text{-Y}_2\text{O}_3$ systems. Auger electron spectroscopy measurements on the electrolyte surfaces of the ZYB sensors show an enrichment of bismuth. Surface concentrations of 10–15 at % Bi are found for all samples. These bismuth rich surfaces influence the response time in the same way as stabilized Bi_2O_3 (see Section 3.1.).

The effect of Bi_2O_3 on t_r also depends on the phase distribution which may occur after the introduction of Bi_2O_3 into ZY. The samples ZYB3 and ZYB4 contain monoclinic ZrO_2 (respectively, 1 and 21 mol%) while ZYB1 and ZYB2 are cubic and monophasic. The higher the amount of monoclinic zirconia the higher the value of E_{act} seems to be.

Monoclinic ZrO_2 is almost non-ion conducting and has a completely different defect structure compared with cubic ZY. This monoclinic second phase reduces the rate of supply or removal of oxygen species from the electrode zone. The response time of these materials is therefore higher than that for cubic monophasic ZYB specimen. An increase in response time was also found when partially stabilized ZrO_2 , containing monoclinic ZrO_2 as a second phase, was used instead of cubic ZrO_2 [15].

3.3. Comparison of platinum and gold electrodes

The effect of the electrode materials (platinum and gold) on t_r was studied for ZY21 and ZYB3 (see Figs. 4 and 5 and Table 2). Surprisingly the use of gold electrodes results in a shorter t_r . We did not find reports in the literature about the effect of gold electrodes on t_r . This effect is now under investigation. Fouletier *et al.* [10] have studied the response behaviour of Pt and Ag electrodes on stabilized ZrO_2 . Here sensors with Ag electrodes have lower response times in the temperature region of 300–700° C.

4. Conclusions

The effect of different sensor materials on the response time after a step change in oxygen partial pressure was investigated. Stabilized Bi_2O_3 has a

larger response time at $T > 500^\circ\text{C}$ than stabilized ZrO_2 , despite the lower electrolyte and electrode resistance of BE solid solutions compared with ZY. The slower response is probably related with the larger low-frequency capacity (pseudo-capacity) of Bi_2O_3 materials. Introduction of Bi_2O_3 into yttria stabilized zirconia results in a longer response time. This effect is more pronounced when a monoclinic ZrO_2 phase is present.

Gold electrodes on yttria stabilized zirconia give a considerably better response time than platinum electrodes.

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