

The transient response of ZrO_2 oxygen sensors to step changes in gas composition

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The transient voltage response of ZrO_2 oxygen sensors was examined following step changes in gas composition. The experiments were performed on a laboratory flow reactor at 600°C . Composition changes between (a) 100% and (b) 1% O_2 in N_2 produced response curves whose symmetry varied between composition steps (a) from low-to-high oxygen and (b) from high-to-low oxygen. This difference is due to the logarithmic dependence of sensor voltage on oxygen partial pressure. Corresponding oxygen partial pressure-time curves, derived from experimental voltage via the Nernst equation, are symmetric with respect to the direction of composition changes. Abrupt transitions are found in voltage-time curves at 600°C following step changes of reactive gases; e.g. from O_2/N_2 mixtures to CO/N_2 , H_2/N_2 or D_2/N_2 mixtures. These voltage-steps represent transitions in stoichiometry of the surface boundary layer on the ZrO_2 sensor. Delay times before the transition also reflect reaction stoichiometry. Response times with O_2/CO , O_2/H_2 and O_2/D_2 follow trends predicted by the kinetic theory of gases. A limited number of experiments were performed to examine the relationships between sensor response and sensor catalytic activity. Poorer oxidation catalytic activity parallels slower response characteristics.

1. Introduction

This paper is concerned with the physicochemical factors that influence the dynamic response characteristics of ZrO_2 oxygen sensors to step changes in gas composition. ZrO_2 sensors are being developed for use in engine control systems on automobiles [1-3]. The sensors consist of a ZrO_2 oxygen-ion conducting electrolyte/membrane separating (a) an oxygen reference gas (air) from (b) a sample gas of unknown composition (automobile engine exhaust). The potential difference, ΔV , which develops across the sensor is related to the oxygen partial pressures, P_{O_2} and P_{O_2}' , in the two gases by the Nernst equation

$$\Delta V = \left(\frac{RT}{4F} \right) \ln [P_{O_2}/P_{O_2}'] \quad (1)$$

Cell voltage is used in an electrical feedback loop to control the air-to-fuel (A/F) ratio entering the engine [4].

The control system operation is influenced by the steady-state relationship between cell voltage and the A/F ratio. In practice, this relationship

can differ from Equation 1 because engine exhaust gases are generally not in internal chemical equilibrium and the effective oxygen partial pressure is ill-defined. The steady-state behaviour of ZrO_2 sensors exposed to nonequilibrium gas mixtures has been explored by Fleming [5, 6], Takeuchi *et al.* [7] and Anderson and Graves [8].

The dynamic (transient) response of ZrO_2 sensor voltage to changes in the bulk gas composition plays a central role in control system operation [4]. These systems operate in a dynamic mode where the A/F ratio is constantly cycled about a predetermined composition. However, physicochemical factors influencing dynamic sensor response have received relatively little attention. Heyne and den Engelsen [9] published theoretical studies of sensor response characteristics. Ross *et al.* [10] have reported dynamic experiments with SO_2 gas-sensing electrodes. Rechnitz *et al.* [11-13] have performed considerable experimental theoretical studies on electrode response to concentration changes in liquid systems. We have recently completed frequency-dependent studies of a ZrO_2 [14] sensor response.

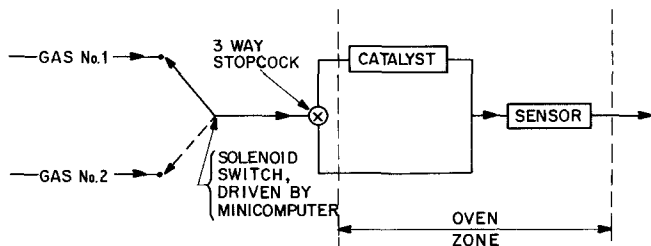


Fig. 1. Schematic diagram of the apparatus used in these experiments. Heavy arrowheads show direction of gas flow through the system.

Transient response experiments on heterogeneous catalysts, although not dealing specifically with concentration cell voltage response, are closely related to such studies. Kobayashi and Kobayashi [15] give a good overview of this work.

Following these previous workers, we produced step concentration changes in a gas flow system and measured sensor voltage as a function of time. An important distinction between the present experiments and earlier studies is our use of concentration changes involving chemically reacting gases; e.g. a step change from 5% CO in N₂ to 1% O₂ in N₂. We also performed some experiments involving step changes between non-reacting gases for comparison purposes; e.g. between pure O₂ and 1% O₂ in N₂.

2. Apparatus

Our experiments were performed on a gas flow system passing through a tube furnace (Fig. 1). The homemade sensor consisted of two platinum electrodes attached to the inner and outer surfaces of a closed tube made from ZrO₂ doped with 8 wt% Y₂O₃ (Zirconia Products). Platinum paste electrodes were used. The inner reference electrode was in contact with air. The outer electrode, exposed to changes in gas composition, covered the rounded end of the tube. This electrode had an approximate geometric area of 0.25 cm² and a thickness of 0.002 cm. Thin platinum wires connected the electrodes to a high-impedance voltmeter.

The ZrO₂ tube was mounted parallel to the gas flow direction. Inlet gas flow emerged from a 1 cm diameter orifice and impinged directly on to the sensing electrode. This minimized the thickness of the surface boundary layers on the electrode.

Experimental voltage response times were typically of the order of 0.3–0.5 s at 600°C. This is roughly five times slower than the reported

response times of commercial ZrO₂ sensors [2].

Our use of platinum paste electrodes may be responsible for this. It should be noted that our laboratory sensors *did not* have the porous spinel coating over the catalyst/electrode surface which is used in many commercial devices [2].

Temperature was measured with an electrically insulated thermocouple placed in the interior of the ZrO₂ tube. Gas composition changes were produced by activating solenoid devices that switched alternate gas streams through the furnace and past the sensor. Solenoids were located in the gas stream some 60 cm before the sensor. At experimental volume flow rates of 16–32 cm³ s⁻¹, this produced delays of 0.2–0.5 s between the solenoid and the sensor. The solenoid switching time was 0.025–0.050 s. At temperatures above 500°C, application of small electrical current pulses to the ZrO₂ cell indicated that the sensor had an electrical (RC) response time of roughly 0.05 s, substantially faster than the composition response times reported below. RC response times increase substantially at temperatures below 500°C. This reflects the larger intrinsic resistance of the ceramic electrolyte at these lower temperatures [3].

The ZrO₂ sensor is extremely sensitive to oxygen partial pressure. For this reason, one measures potential differences corresponding to trace O₂ impurities in nominally pure gases. For example, we typically measure a potential difference of roughly 180 mV at 600°C with 'high-purity' nitrogen: this corresponds to an O₂ level of 13 ppm.

A Minc minicomputer system (Digital Equipment Corp.) was used to store voltage–time measurements and to convert them into corresponding partial pressure time data.

3. Experimental results and discussion

The present experiments are concerned with the response of ZrO₂ sensors to step changes in

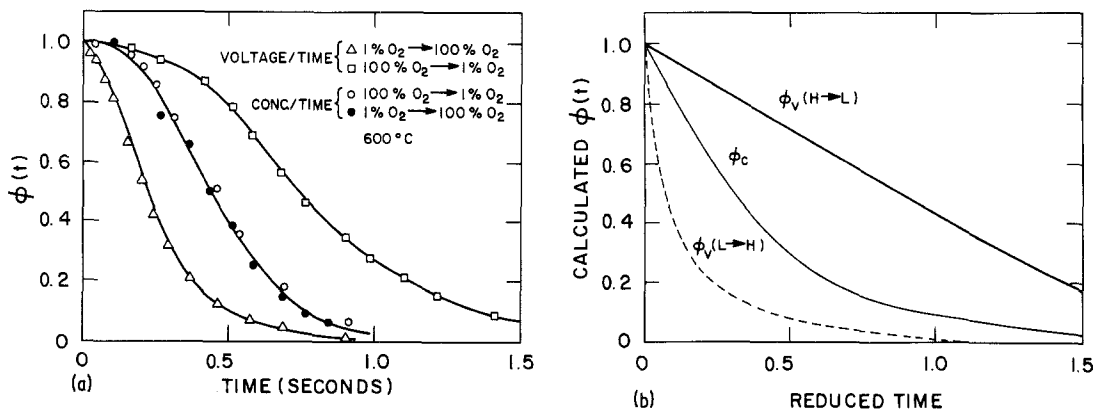


Fig. 2. (a) Experimental ϕ_v -time curves. Note asymmetry in $\phi_v(t)$ between step concentration changes in opposite directions. There is no asymmetry in corresponding $\phi_c(t)$ curves. (b) calculated ϕ_v , ϕ_c -time curves (Equation 3) showing the same effects as those seen experimentally. All data were obtained at 600° C.

gaseous oxygen concentrations. In interpreting the data, it is important to distinguish between concentration changes involving (a) reacting and (b) non-reacting gases.

Fig. 2 shows representative data for the non-reactive O₂/N₂ system at 600° C. In this and in subsequent figures, data are presented in terms of normalized functions, $\phi_v(t)$ and $\phi_c(t)$, defined by

$$\phi_v(t) \equiv \frac{[V(t) - V(\infty)]}{[V(0) - V(\infty)]} \quad (2)$$

and

$$\phi_c(t) \equiv \frac{[P_{O_2}(t) - P_{O_2}(\infty)]}{[P_{O_2}(0) - P_{O_2}(\infty)]} \quad (3)$$

The parameter $V(t)$ in Equation 2 is the experimental cell voltage at time t . Oxygen partial pressures, $P_{O_2}(t)$, in Equation 3 are derived from experimental $V(t)$ values via Equation 1. $V(0)$ and $V(\infty)$ are voltages at $t = 0$ and $t = \infty$, respectively. $P_{O_2}(0)$ and $P_{O_2}(\infty)$ are the corresponding oxygen partial pressures.

As shown in Fig. 2, there is a marked asymmetry between the voltage-time [$\phi_v(t)$] curves obtained going from (a) high-to-low and (b) low-to-high oxygen concentrations. In neither case does $\phi_v(t)$ follow simple kinetics. Typically, there is a rapid initial decay followed by a slower long-time 'tail'. However, if one uses Equation 1 to compute oxygen partial pressures from experimental emf values, the resulting $\phi_c(t)$ curves are symmetric with respect to high-to-low or low-to-high concentration changes. A qualitative measure of response asymmetry is obtained if one first (a)

averages the $\phi(t)$ curves measured following composition steps in opposite directions, then (b) computes the root mean square (rms) deviations of the individual curves from this average. For experimental data between 0.1 and 1.0 s, this procedure yields rms deviations of 0.02 and 0.246 for the oxygen partial pressure-time and the voltage-time data, respectively.

Ross *et al.* [10] reported similar transient asymmetry in studies of gas electrodes. They recognized that electrode emf measures partial pressure in the electrode surface boundary layer, and interpreted their response data in terms of a first-order exchange process between two regions: (a) a bulk gas region where step concentration changes were produced experimentally, and (b) a boundary layer region of uniform concentration. A bulk gas/boundary layer exchange coefficient, k_m , characterizes the response of boundary layer concentration to bulk gas composition changes. Similar kinetic schemes are commonly used to analyse catalytic experiments [15]. The exact nature of the boundary layer is poorly defined: it is partially governed by the porosity of the surface; partially by the dimensions of the stagnant surface layer in a flowing system. Recast in terms of boundary layer oxygen partial pressure, the analysis of Ross *et al.* [10] yields a response curve of the form

$$\frac{P_{O_2}(t) - P_{O_2}(\infty)}{P_{O_2}(0) - P_{O_2}(\infty)} = \exp(-k_m t). \quad (4)$$

Here $P_{O_2}(t)$ is the boundary layer oxygen partial pressure at time t . $P_{O_2}(0)$ is the initial boundary

layer oxygen partial pressure, which is identical to the initial bulk gas partial pressure. $P_{O_2}(\infty)$, the final partial pressure of oxygen in the boundary layer is identical to the final bulk gas oxygen content. Equation 4 is clearly symmetric with respect to high-to-low or low-to-high changes in O_2 partial pressure. The logarithmic dependence of cell emf upon partial pressure produces an asymmetry in voltage-time responses that increases with the magnitude of the partial pressure difference between the initial and final states. Voltage response is always slower going from high-to-low than from low-to-high oxygen partial pressures. Calculated curves showing these effects are presented in Fig. 2b.

The shape and duration of the response curves reflect a convolution between the bulk gas/boundary layer exchange process and (a) the shape of the bulk gas composition front produced by solenoid switching, and (b) the internal electrochemical time response of the sensor. It is unclear whether these two factors are responsible for differences between the shapes of experimental and calculated response curves. Alternatively, it may be that a more sophisticated kinetic analysis is required to fit experimental ϕ_v and ϕ_c curves qualitatively. This might involve consideration of a second-order diffusion process to allow for concentration gradients in the boundary layer perpendicular to the electrode surface. Better deconvolution of experimental factors from the exchange process is needed before use of more sophisticated kinetics is justified.

Experimental response times for ϕ_c were in the range 0.3–0.5 s. For comparison purposes, one estimates a 0.05 s response time from simple diffusion theory [$\tau = \langle X^2 \rangle / (2D)$], assuming the diffusion constant for oxygen in air is $D = 0.92 \text{ cm}^2 \text{ s}^{-1}$ [16] and the effective mean square boundary layer thickness, $\langle X^2 \rangle$, is 0.09 cm^2 .

Step concentration changes between reactive gases produce response characteristics that differ substantially from those described above. Fig. 3 shows representative $\phi_v(t)$ data for 600°C for step concentration changes from 5% CO in N_2 to varying concentrations of O_2 in N_2 . There is an abrupt voltage transition at a time Z which increases with decreasing oxygen concentrations. Corresponding $\phi_c(t)$ curves exhibit similar tran-

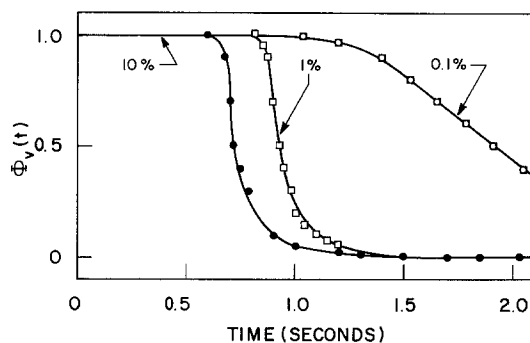


Fig. 3. $\phi_v(t)$ response curves for reactive gases: initial gas was 5% CO in N_2 ; final gas contained O_2 in N_2 at the concentrations shown on the figure. The initial induction period includes a time delay for gas flow between the solenoid switch and the sensor. All data were obtained at 600°C .

sitions. These induction periods and transitions do not occur with non-reacting gases.

The physical reason for this difference is clear. With non-reacting gases, response characteristics reflect only bulk gas/boundary layer exchange kinetics (mass transfer). Step composition changes involving reacting gases produce reactions in the boundary layer that provide the basic mechanism for concentration change and voltage response. Extending the analysis of Ross *et al.* [10] to the CO/ O_2 system, we consider three coupled processes:

$$\frac{dP_{O_2}}{dt} = -k_m [P_{O_2} - P_{O_2}(\text{bulk})] - W \quad (5a)$$

$$\frac{dP_{CO}}{dt} = -k_m [P_{CO} - P_{CO}(\text{bulk})] - 2W \quad (5b)$$

$$\frac{dP_{CO_2}}{dt} = -k_m [P_{CO_2} - P_{CO_2}(\text{bulk})] + 2W. \quad (5c)$$

These expressions characterize (a) diffusive exchange of three gases between bulk gas and boundary layer regions together with (b) chemical reaction only in the boundary layer. The reaction is presumed to occur on the electrode surface at a rate much faster than that of the mass transfer process: under these conditions, boundary layer concentrations correspond to a type of constrained equilibrium. The overall reaction velocity, W , is given by

$$W = k_f P_{O_2} P_{CO}^2 - k_b P_{CO_2}^2. \quad (6)$$

The parameters $P_{O_2}(\text{bulk})$, $P_{CO}(\text{bulk})$ and $P_{CO_2}(\text{bulk})$ in Equation 5 refer to partial pressures in the bulk gas. For convenience, all gas exchange coefficients (k_m) are assumed to be identical in Equation 5. We now define two new variables, x and y :

$$x \equiv 2(P_{O_2} + P_{CO_2}) + P_{CO} \quad (7a)$$

$$y \equiv P_{CO} + P_{CO_2} \quad (7b)$$

and find

$$dx/dt = -k_m[x - x(\text{bulk})] \quad (8a)$$

$$dy/dt = -k_m[y - y(\text{bulk})] \quad (8b)$$

from which $x(t)$ and $y(t)$ are readily determined following step changes in bulk gas composition. If the surface reaction rates are fast enough to maintain a quasi-chemical equilibrium in the boundary layer, $W \approx 0$, and $P_{O_2}(t)$ can be determined from the roots of

$$P_{O_2} = \left(\frac{k_b}{k_f} \right) \left(\frac{[(x-y) - 2P_{O_2}]^2}{[2P_{O_2} + (2y-x)]} \right). \quad (9)$$

This expression follows directly from Equations 6 and 7, using the definitions of x and y . The roots of Equation 9 can be approximated to

$$P_{O_2} \approx [P_{O_2}(\text{bulk}) - \frac{1}{2}P_{CO}(\text{bulk})];$$

$$P_{O_2}(\text{bulk}) > \frac{1}{2}P_{CO}(\text{bulk}) \quad (10a)$$

and

$$P_{O_2} \approx \left(\frac{k_b}{k_f} \right) \left(\frac{[2P_{O_2}(\text{bulk}) + P_{CO_2}(\text{bulk})]^2}{[P_{CO}(\text{bulk}) - 2P_{O_2}(\text{bulk})]} \right);$$

$$P_{O_2}(\text{bulk}) < \frac{1}{2}P_{CO}(\text{bulk}). \quad (10b)$$

There is an abrupt change in P_{O_2} at a stoichiometry that results in a voltage step in $V(t)$. This occurs when $(x - 2y) = 0 = (x_\infty - 2y_\infty) + [(x_0 - 2y_0) - (x_\infty - 2y_\infty)] \exp[-k_m Z]$; i.e. at a transition time Z where

$$Z \equiv \frac{1}{k_m} \ln(1+R)$$

$$= \frac{1}{k_m} \ln \left[1 + \frac{[P_{CO}(\text{bulk}) - 2P_{O_2}(\text{bulk})]_0}{[2P_{O_2}(\text{bulk}) - P_{CO}(\text{bulk})]_\infty} \right]. \quad (11)$$

Figure 4 compares this function with experimental results on the O₂/CO system at 600° C. Agreement is satisfactory at high final O₂ levels. Mass transfer coefficients obtained from the slope of $Z - \log(1+R)$ plots range around 0.3 s; corresponding values for non-reactive gases are approxi-

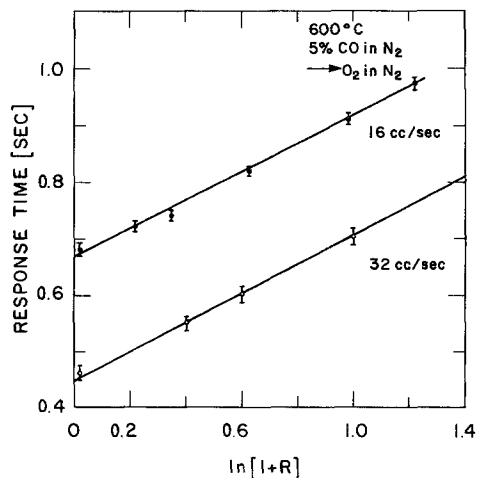


Fig. 4. Comparison of experimental Z values with $\log(1+R)$ as described in the text. The linear relationship indicates the validity of kinetic analysis. The intercepts at $\log(1+R) = 0$ define the flow-rate-dependent time delay between the solenoid switch and the sensor. All data were obtained at 600° C.

mately 0.4 s. There is poorer agreement between experiment and Equation 11 at low final O₂ partial pressures where the bimolecular O₂-CO reaction is slow and gas diffusion no longer limits overall reaction kinetics.

The time required for cell emf to change from $\phi_v(t) = 0.9$ to 0.1 has been taken as a convenient measure of electrode response [10]. This can be misleading in the case of composition changes between reacting gases. For systems involving species that react almost irreversibly with oxygen; e.g. CO, H₂ etc., most of the voltage change occurs close to the time when a stoichiometric composition exists in the boundary layer. The time required for the voltage transition may be significantly shorter than the gas diffusion exchange time.

Asymmetry between response curves obtained in going from (a) high-to-low and (b) low-to-high oxygen partial pressures is found with reactive gases. It occurs in both voltage-time and concentration-time response functions. As implicitly stated in Equation 11, this asymmetry is governed by the relative concentrations of oxygen and reactant gas before and after the step concentration change. With reactive gases, the slower response function may occur following either a high-to-low or a low-to-high change in oxygen

Table 1. Transition times, Z (s) for step composition changes between 5% O_2 in N_2 and (a) 5% H_2 in N_2 ; (b) 5% D_2 in N_2 ; (c) 5% CO in N_2 . Temperature, 600° C; flow rate, 16 $cm\ s^{-1}$. Data corrected for time delay between solenoid and sensor

Gas	5% H_2	5% D_2	5% CO
$O_2 \rightarrow$ Gas	0.15	0.30	0.80
Gas $\rightarrow O_2$	0.20	0.20	0.20

partial pressure. For example, the experimental transition time ratio for 5% O_2 –5% CO at 600° C was 0.25; the calculated ratio from Equation 11 is 0.59.

Relationships between gas mass diffusion coefficients and sensor response were examined. The kinetic theory of gases [15] predicts that diffusion coefficients should vary as $[M]^{-1/2}$, where M is the gas molecular weight. On this basis, sensor response following composition changes involving oxidation of H_2 , D_2 and CO should reflect diffusion exchange in the ratio 3.7 : 2.6 : 1.0. Generalization of Equation 11 to gases with unequal gas diffusion coefficients is complex and will not be treated here. However, it is clear by analogy to Equation 5 that increasing the diffusion exchange of the reactant species should reduce the transition time. As indicated in Table 1, experimental transition times from 5% O_2 to (a) 5% H_2 , (b) 5% D_2 , (c) 5% CO in N_2 follow this trend.

There have been several reports that long-term operation changes the experimental steady-state voltage–composition relationships of ZrO_2 sensors [4, 5]. Strong experimental evidence links these changes to degradation of the catalytic activity of the sensor electrode. When exposed to non-equilibrium gas mixtures, the surface electrode serves both as a catalyst promoting oxygen/reactant equilibration in the surface boundary layer and as a monitor of oxygen partial pressure [1, 5–8]. Boundary layer oxygen partial pressures approach values corresponding to chemical equilibrium in the bulk gas under conditions of mass transfer limited kinetics. In contrast, boundary layer oxygen partial pressures do not correspond to equilibrium in the bulk gas when surface reaction rates are slow or comparable to gas diffusion exchange rates. Under the latter circumstances, the sensor develops a non-equilibrium voltage.

A limited number of experiments were performed to examine the relationships between catalytic activity and sensor response times. These involved measurements of sensor response with and without a secondary catalyst in the gas stream before the ZrO_2 sensor. The secondary catalyst, consisting of platinum supported on $\gamma-Al_2O_3$, had a greater capacity than the sensor for promoting chemical equilibration in the gas stream: this reduced the need for the sensor to function as an oxidation catalyst. Step concentration changes were made between (a) a mixture containing a stoichiometric excess of oxygen [6% O_2 + 5% CO in N_2] and (b) a mixture containing a stoichiometric excess of carbon monoxide (2% O_2 + 5% CO in N_2).

Figure 5 shows that (a) the final steady-state voltage is substantially larger, by roughly 100 mV, when the gases are pre-equilibrated over the secondary catalyst and (b) sensor response is faster with the secondary catalyst present.

The first observation is readily understood. The secondary catalyst effectively equilibrates the CO – O_2 mixture. The sensor electrode need not function catalytically, and measured voltage [800 \pm 30 mV] is close to that predicted thermodynamically (730 mV for a 2% O_2 –5% CO mixture at 600° C). The limited catalytic activity of the sensor electrode results in a lower cell voltage when pre-equilibration over the secondary catalyst is not used.

Turning to the transient experiments, it should be noted that boundary layer oxygen partial pressures are very low throughout both experiments. This is demonstrated by the substantial cell voltage; e.g. 500 mV corresponds to 10^{-12} atm O_2 at 600° C. For this reason, one can use small-signal linear response theory to compute kinetics. First, we follow Langmuir [17] and express a surface-reaction limited reaction velocity as

$$W = \frac{kP_{CO}P_{O_2}^{1/2}}{(1 + \alpha P_{CO} + \beta P_{O_2}^{1/2})^2} \quad (12)$$

In Equation 12, α and β are parameters characterizing adsorption and desorption, while k is a measure of surface catalytic activity. Now writing $P_{O_2}(t) = A + a(t)$, expansion about the steady-state O_2 partial pressure in the boundary layer, A , gives

$$\frac{dP_{O_2}}{dt} = \frac{da}{dt} = - \left\{ k_m [A - P_{O_2}(\text{bulk})] + \frac{kP_{CO}A^{1/2}}{(1 + \alpha P_{CO} + \beta A^{1/2})^2} \right\} - \left[k_m + \frac{kP_{CO}A^{-1/2}}{(1 + \alpha P_{CO} + \beta A^{1/2})^2} \right] a. \quad (13)$$

The first set of terms, in braces, vanishes: this is the condition for steady-state. The rate constant, $\{k_m + [kP_{CO}A^{-1/2}/(1 + \alpha P_{CO} + \beta A^{1/2})^2]\}$, decreases with (a) increasing boundary layer oxygen, A ; and (b) decreasing surface activity, k .

The secondary catalyst can be viewed as either increasing the effective sensor catalytic activity or as decreasing the steady-state boundary layer oxygen partial pressure. Both factors decrease the sensor response time in accord with the experiments.

4. Conclusions

1. Voltage-time response curves were observed for ZrO₂ sensors exposed to step changes in gas composition. Concentration steps from low-to-high oxygen partial pressure produced faster voltage response than high-to-low concentration steps. This can be understood as a bulk gas/boundary layer exchange process where oxygen partial pressure is the relaxing variable. Asymmetry arises from the logarithmic dependence of voltage on oxygen partial pressure.

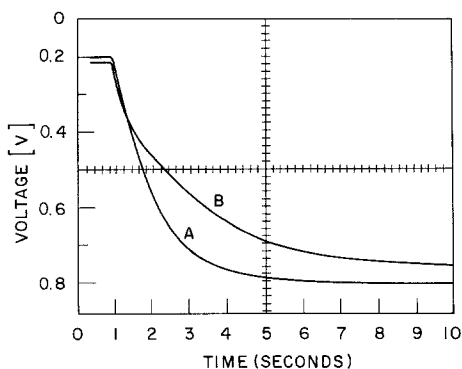


Fig. 5. Comparison of oscilloscope voltage response going from (a) 6% O₂/5% CO in N₂ to (b) 2% O₂/5% CO in N₂. Curve A: with secondary catalyst; curve B: without secondary catalyst. Measurements were obtained at 600° C.

2. Response curves following concentration steps involving reacting gases differ from those where no reaction is involved. These differences can be understood in terms of time-dependent boundary layer oxygen partial pressures.

3. The catalytic activity of the surface electrode influences experimental response times.

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