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Hysteresis effects with ZrO_2 oxygen sensors exposed to non-equilibrium oxygen-hydrocarbon mixtures

J. E. ANDERSON, Y. B. GRAVES

Engineering and Research Staff, Research Ford Motor Company, Dearborn, Michigan 48121, USA

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Hysteresis effects are reported for ZrO_2 oxygen sensors exposed to non-equilibrium oxygen/hydrocarbon gas mixtures. With oxygen/toluene at 800° C, voltage–composition curves differ following composition changes (a) from excess oxygen to excess toluene and (b) from excess toluene to excess oxygen. A catalysis model is developed to account for this behaviour: the Thiele modulus of the catalyst/electrode is presumed to differ under (a) net oxidizing and (b) net reducing conditions. Large scale voltage fluctuations, sometimes exceeding 400 mV, were observed in experiments with oxygen/isobutane mixtures at 600° C. This behaviour is analysed in terms of a kinetic model involving stochastic variations of relative mass transfer coefficients of oxygen and isobutane.

1. Introduction

This research is part of a program directed at determining characteristics of ZrO_2 oxygen sensors exposed to non-equilibrium gas mixtures [1–5]. The sensors are essentially high temperature ($T > 450°$ C) oxygen concentration cells [6]. Surface electrodes, typically made from platinum, are attached to opposite sides of a ZrO_2 solid-state 'membrane'. The electrodes not only measure e.m.f. differences across the membrane, but also catalyse chemical reactions of non-equilibrium gas mixtures.

ZrO_2 sensors have been developed for feedback control applications on automobiles [7–9]. Here they are exposed to non-equilibrium engine exhaust gases.

Cell voltage is related to oxygen partial pressures on opposite sides of the ZrO_2 membrane by the Nernst equation:

$$V = -(RT/4F)\ln(P_{O_2}/P_{O_2}') \qquad (1)$$

In this expression P_{O_2} and P_{O_2}' refer to the oxygen partial pressures in a sample and a reference gas, respectively. It should be emphasized that these partial pressures refer to concentrations within surface boundary layers at the solid electrolyte/gas interfaces. In most studies, air is used as the oxygen reference: we follow this tradition in the present work.

The sensor electrodes are very small compared to the bulk gas volume; in fact, bulk volumes become infinite when gases flow at high rates past the sensor. In this case, surface catalysis only influences gas concentrations within boundary layers adjacent to the electrode surfaces. Steady-state boundary layer concentrations are dictated by the Thiele modulus; i.e. the relative rates of (a) chemical reactions in the boundary layer, and of (b) gas diffusion between the boundary layer and bulk gas regions. Following Equation 1, variations in the boundary layer composition are reflected in the cell e.m.f. [1, 10].

For "rich" non-equilibrium gas mixtures, i.e. mixtures containing less than a stoichiometric amount of oxygen, certain generalizations can be made relating cell voltage to electrode catalytic activity [1–3]. Because of their greater efficiency in promoting oxidation reactions, high-activity surfaces effectively remove more O_2 from the boundary layer than do lower-activity surfaces. For this reason, high-activity surfaces generate higher cell e.m.f.'s (smaller $[P_{O_2}/P_{O_2}']$ ratios) than lower activity catalysts [1–3, 10–13]. It is noteworthy that the surface activity differences seen in these e.m.f. measurements are trivial by conventional catalysis standards. For example, a non-equilibrium oxygen/hydrocarbon mixture

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containing 0.1 atm. oxygen may generate e.m.f.'s of 800 and 600 mV with high- and low-activity electrodes, respectively; this corresponds to 10^{-15} Pa residual surface O_2 in one case and 10^{-10} Pa in the other.

With this background, it is readily seen that changes in the Thiele modulus produced by oxidation products should be reflected in the cell voltage. Obviously both reversible and irreversible changes are possible. These include effects produced by catalyst poisoning and/or by the generation of non-volatile products that interfere with the diffusive exchange between boundary layer and bulk gas regions.

The present report gives two examples of unusual experimental cell voltage–gas composition curves that can be related to reversible changes in the electrode Thiele modulus.

2. Experimental details

Oxygen sensors were fabricated from tubes of ZrO_2 doped with 8 wt% Y_2O_3 (Zircoa Products). Platinum paste electrodes with a surface area of 0.25 cm^2 were attached to inner and outer tube surfaces. The sensor was housed in a quartz tube and placed in a tube furnace. Furnace temperatures were measured with a thermocouple. Gases were mixed externally and travelled in a flow tube past the sensor.

Reagent grade chemicals were used. Rotometers were used to control nitrogen and isobutane flow rates. Nitrogen saturated with toluene was prepared by bubbling nitrogen through liquid toluene. The resulting toluene concentration in the gas phase was determined by oxygen titration. Oxygen flow rates were determined with a Matheson Model 8240 Controller. This unit was modified so that O_2 flow rates can be defined by an external voltage, rather than by the voltage output from an internal potentiometer. Triangular voltage waveforms from a PAR Model 175 Programmer were used to produce O_2 flow rate variations of 4×10^{-4} cm^3 s^{-2}. A total gas flow rate of 13 cm^3 s^{-1} was used.

3. Results and discussion

Experimental and calculated cell voltage–λ curves are shown in Figs. 1 to 5. The parameter λ represents the oxygen/fuel ratio divided by the corresponding ratio at stoichiometry. The oxygen partial pressure entering the system was varied in the experiments.

Fig. 1 shows experimental data for CO. This represents an idealized system. The cell voltage passes from a high voltage plateau at $\lambda < 1$ to a low voltage plateau at $\lambda > 1$. Experimental traces obtained going from high-to-low and low-to-high oxygen partial pressures can be superimposed. Voltage fluctuations (noise) are less than 5 mV rms throughout the sweep cycle. Toluene–nitrogen–oxygen and butane–nitrogen–oxygen mixtures generated voltage–λ traces similar to Fig. 1 when the mixtures were equilibrated over a high-surface-area platinum catalyst prior to sensor detection.

Hysteresis effects were observed with many hydrocarbon–oxygen–nitrogen mixtures when the gases were not equilibrated over a secondary catalyst prior to sensor detection. Fig. 2, showing experimental data obtained with toluene, typifies 'simple hysteresis'; i.e. hysteresis without massive voltage fluctuations. The flow system initially was under oxidizing conditions ($\lambda \gg 1$). Subsequent reduction of the input oxygen partial pressure at a constant rate produced a voltage maximum slightly below $\lambda = 1$. Lowering P_{O_2} further resulted in a plateau voltage some 200 mV less than the expected value with a high activity electrode/catalyst. No corresponding voltage maximum was observed on the return sweep, when P_{O_2} was increased from $\lambda \ll 1$ to stoichiometry. Voltage–λ traces have the same general shape if programmed P_{O_2} changes occur at slower rates: the voltage maxima become sharper under these conditions.

It has been reported previously [1–3, 10–13] that ZrO_2 sensor voltages developed with non-equilibrium gas mixtures are sensitive to the Thiele modulus of the electrode/catalyst. This sensitivity provides a likely explanation for the observed hysteresis: one need only assert that the Thiele modulus changes going from rich ($\lambda \ll 1$) to lean ($\lambda \gg 1$) conditions. The following model illustrates this.

For simplicity, it will be assumed that the boundary layer partial pressure of the excess component always adopt its equilibrium value independent of the Thiele modulus. This means

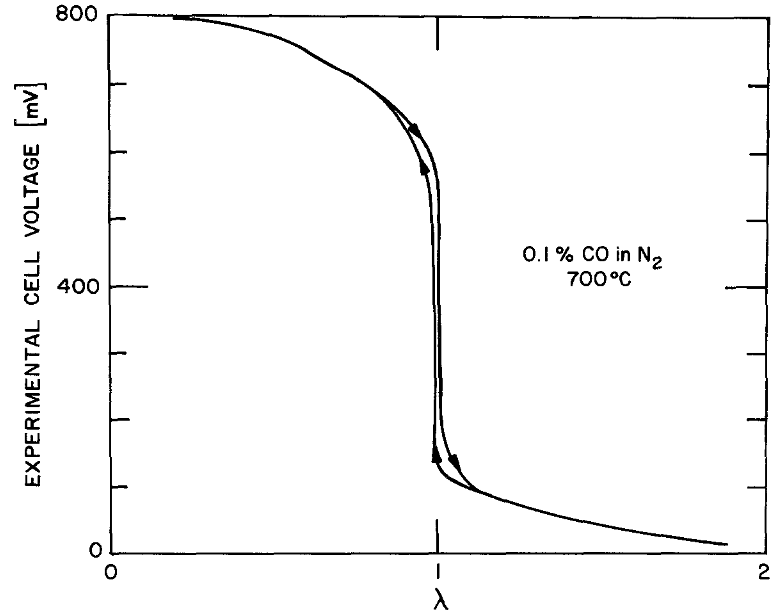

Fig. 1. Experimental voltage–composition curves for CO/O$_2$ mixtures at 700° C. Arrows indicate the sweep direction.

that boundary layer O$_2$ is in equilibrium when $\lambda > 1$ and that hydrocarbon oxidation produces equilibrium amounts of CO and CO$_2$ when $\lambda < 1$. This is consistent with the observation that even a low-activity electrode/catalyst removes more than 99.99% of the boundary layer O$_2$ under rich conditions. With $\lambda < 1$, the residual boundary layer oxygen partial pressure, (O$_2$), can be obtained from the steady-state solution of

$$\mathrm{d}\,(\mathrm{O_2})/\mathrm{d}t = -k_{\mathrm{D}}([\mathrm{O_2}] - [\mathrm{O_2}[\mathrm{bulk}]]) - k_{\mathrm{r}}([\mathrm{O_2}][\mathrm{CO}]^2 - K_{\mathrm{E}}[\mathrm{CO_2}]^2) \quad (2)$$

The rate constant k_{D} characterizes oxygen diffusion (exchange) between the bulk gas and the boundary layer, k_{r}, the rate of boundary layer O$_2$/CO reaction and K_{E}, the equilibrium for

$$2\,\mathrm{CO} + \mathrm{O_2} \rightleftharpoons 2\,\mathrm{CO_2}.$$

O$_2$ (bulk) corresponds to the bulk gas oxygen partial pressure, assumed to be a known input parameter. [CO] and [CO$_2$] refer to boundary layer values obtained from bulk oxygen and hydrocarbon concentrations. Rearrangement of Equation 2 gives

$$[\mathrm{O_2}] = \frac{R[\mathrm{O_2}(\mathrm{bulk})] + k_{\mathrm{E}}[\mathrm{CO_2}]^2}{R + [\mathrm{CO}]^2} \quad (3)$$

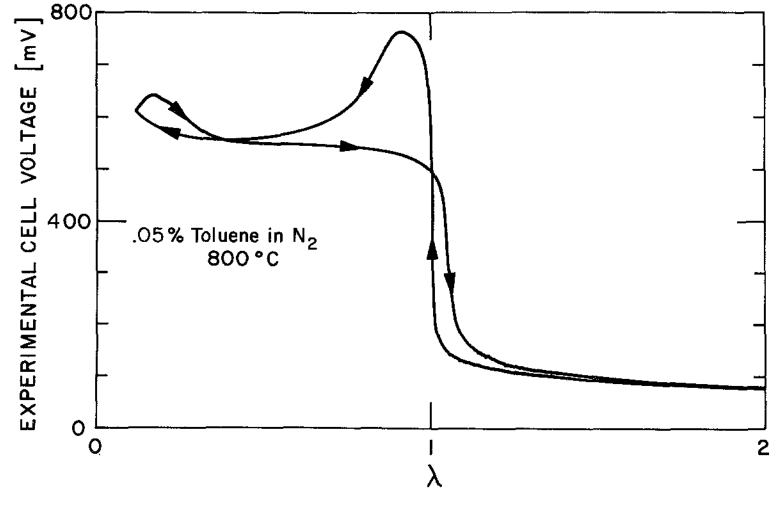

Fig. 2. Experimental voltage–composition curves for toluene/O$_2$ at 800° C.

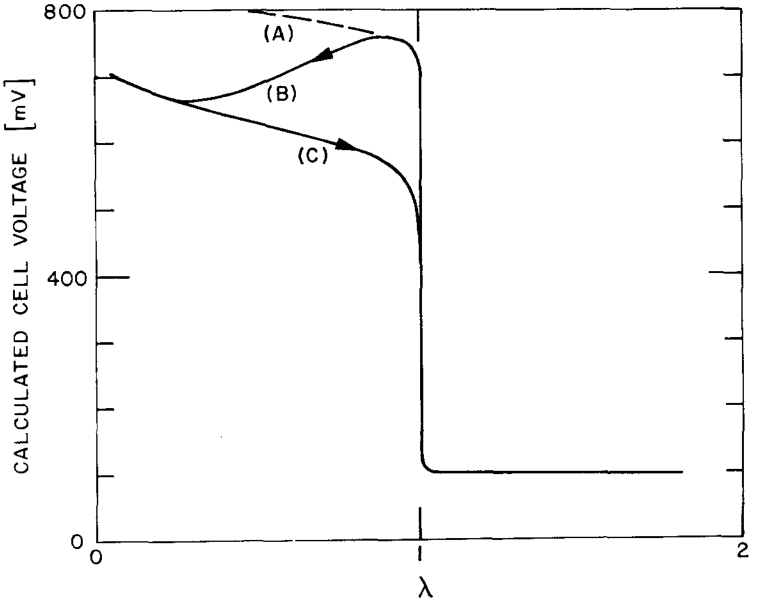

Fig. 3. Calculated voltage–composition data generated by the model of Equations 3 to 5. Curves (A) to (C) represent fast, intermediate, and slow composition sweeps relative to the rate of surface activity change, respectively. Curves (A) and (C) coincide for high-to-low and low-to-high λ sweeps. The arrows show the sweep direction for curve (B) which coincides with (C) during the return sweep.

where we have defined an effective Thiele modulus $R = (K_D/k_r)$. R is assumed to have the value R_1 under steady-state reducing conditions and the value R_2 under steady-state oxidizing conditions. At any instance the instantaneous value of R is determined by the kinetic (relaxation) equations

$$dR/dt = -k_s(R - R_1) \qquad (\lambda < 1) \quad (4)$$

$$dR/dt = -k_s(R - R_2) \qquad (\lambda > 1). \quad (5)$$

The rate of Thiele modulus change is characterized by k_s. Equations 3 to 5 may be solved for time-dependent $[O_2]$ values as a function of (a) constant bulk hydrocarbon concentration; (b) time-dependent $[CO_2(\text{bulk})]$; (c) values of R_1, R_2 and k_s. These $[O_2]$ values are converted to cell e.m.f. via Equation 1. It should be noted that the model assumes that boundary layer concentrations readjust to bulk gas composition changes faster than does the surface activity parameter, R, to excursions through stoichiometry.

Fig. 3 shows calculated voltage–λ curves for various sweep rates back and forth through stoichiometry. It can be seen that the calculated results qualitatively reproduce the main features of the experimental data shown in Fig. 2. At slow sweep rates, the Thiele modulus switches over a narrow composition range near $\lambda = 1$. The resulting voltage–λ curve (C) combines a 'rich' region ($\lambda > 1$) with $R(t) = R_1$ and a 'lean' region ($\lambda < 1$) with $R(t) = R_2$. Time-dependent changes in Thiele modulus are seen with faster sweep rates (curve (B)): this is characterized by a voltage maximum as λ is reduced from $\lambda > 1$ to $\lambda < 1$. There is no corresponding voltage maximum going from low-to-high oxygen because the boundary layer must contain excess oxygen before the $R_1 \rightarrow R_2$ transition is made. The calculations suggest a third region corresponding to fast sweep rates (curve (A)). Here the Thiele modulus does not have sufficient time to respond to change boundary layer stoichiometry, and $R(t)$ effectively remains equal to R_2 throughout both high-to-low and low-to-high sweeps of oxygen partial pressure. This regime was not seen experimentally: time-delays between the point of O_2 injection and sensor detection complicate the analysis of the experimental voltage–λ curves when rapid changes of oxygen partial pressure are attempted.

Fig. 4 shows experimental results with isobutane. There is noticeable hysteresis between data taken on high-to-low and low-to-high oxygen partial pressure sweeps. It seems likely that this is also caused by changes in the effective Thiele modulus as a function of the boundary layer composition. However, large-scale voltage fluctuations (sometimes exceeding 400 mV in magnitude) are the most striking characteristics of the experiments performed with isobutane and other alkanes (data not shown). These voltage fluctuations are not affected by sweeping the external oxygen

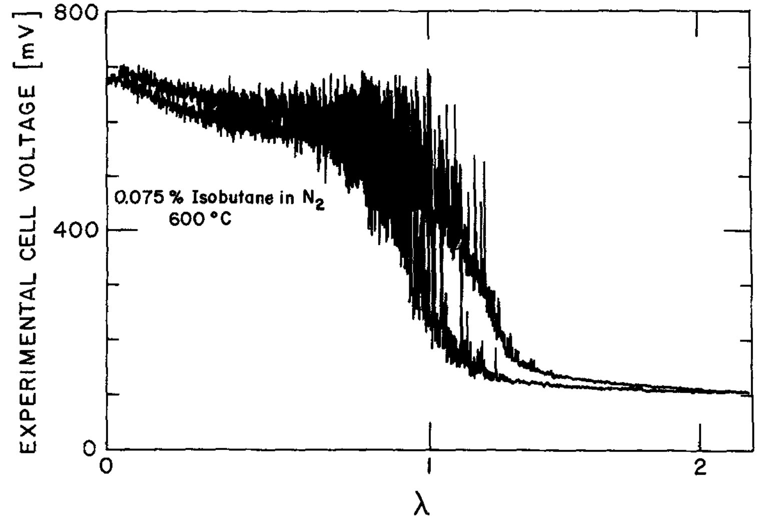

Fig. 4. Experimental voltage–composition curves for isobutane/oxygen at 600° C.

partial pressure: they persist indefinitely at a constant oxygen/hydrocarbon composition in the flow tube. Logothetis and Hetrick [14, 15] reported regular periodic voltage oscillations when ZrO_2 sensors are exposed to non-equilibrium CO–O_2 mixtures at low temperatures. They related their observations to isothermal periodic composition oscillations known to occur during CO oxidation on platinum. Voltage fluctuations with isobutane and other alkanes seem qualitatively different from CO oscillations. First, voltage fluctuations occur at much higher temperatures. Second, they persist over a wider range of inlet composition than do the CO oscillations. Third, the voltage oscillations appear to be totally aperiodic: spectrum analysis of the fluctuations showed no preferred frequencies. Finally, as shown in Fig. 4, the magnitude of the fluctuations is considerably larger near stoichiometry ($\lambda = 1$) than under strongly oxidizing ($\lambda \gg 1$) or strongly reducing ($\lambda \ll 1$) conditions. These features were observed, to varying degrees, with all alkane fuels studied. We noted no obvious correlations between the molecular structure of particular alkanes and the magnitude of voltage fluctuations. The size of the voltage fluctuations was influenced by the temperature and the flow rate past the sensor. Different ZrO_2 sensors all exhibited voltage fluctuations with alkane fuels, but the fluctuation magnitude varied from sensor to sensor.

Previous studies [3, 5, 10] of ZrO_2 sensors exposed to non-equilibrium gas mixtures show that the location of the voltage step along the λ-axis is sensitive to the relative rates at which the oxygen and the combustible fuel are supplied to the catalyst/electrode surface. A step in the voltage curves occurs at $\lambda = [k(\text{fuel})/k(\text{oxygen})]$, where k(fuel) and k(oxygen) are the effective exchange rates between the bulk gas and the surface layer of the electrode. Experimental data suggest that these effective rate constants range between the values for convective flow (where both rates are equal and the voltage step occurs at $\lambda = 1$) to values for diffusive flow (inverse variation with the square root of molecular mass and a voltage step shifted away from the bulk gas stoichiometry) [1, 3, 5, 10]. As reported elsewhere [3], the net effect of a non-unity $[k(\text{fuel})/k(\text{oxygen})]$ ratio is to shift the effective boundary layer λ away from the bulk gas value: under the common situation of mass transfer limited kinetics all equations retain the same form in terms of a boundary layer λ. We developed a kinetic model based on stochastic fluctuations of λ in the boundary layer (i.e. based on stochastic changes of the $[k(\text{fuel})/k(\text{oxygen})]$ ratio) to account for the isobutane data. Specifically, we considered changes between (a) the bulk value, λ_0; and (b) $\lambda_0 + \Delta\lambda$, where $\Delta\lambda$ is an arbitrary input parameter. The time-interval between alternating transitions was determined by random sampling from an exponentially-distributed set of waiting times. Results of this modelling study, shown in Fig. 5, are in fair agreement with the experimental results shown in Fig. 4. Other

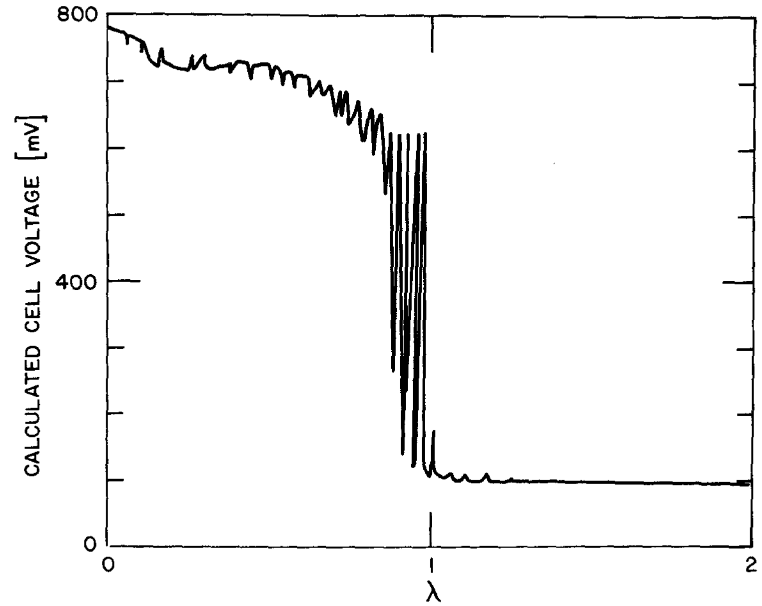

Fig. 5. Calculated voltage–composition data based on stochastic variations of the [k(fuel)/k(oxygen)] exchange rate ratio.

attempts to mimic Fig. 4 through stochastic variations of surface activity, i.e. stochastic variations of R, were totally unrewarding.

Both of the above models are admittedly unsatisfying since they provide no detailed description of the underlying causes for the variations in surface activity. Several mechanisms were considered including (a) changes produced by adsorption/desorption of primary products, e.g. carbonaceous matter; (b) oxidation/reduction of the catalytic metal surface; (c) changes in boundary layer/bulk gas diffusion exchange caused by a λ-dependent pore structure. Further experiments are required to establish these, or other mechanisms. Whatever the underlying mechanism, the models show that variations in the surface activity or relative exchange rates can account for the time-dependent phenomena observed when non-equilibrium oxygen/hydrocarbon mixtures interact on platinum electrode/catalysts attached to ZrO_2 oxygen sensors.

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