Mass transfer effects on ZrO_2 oxygen concentration cells exposed to non-equilibrium $H_2−O_2$ mixtures

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We report further studies of ZrO_2 oxygen concentration cells exposed to non-equilibrium gas mixtures. Substantial shifts of cell voltage–(H_2/O_2) composition curves are produced by changes in the gas flow rate past the cell. At high flow rates, there is an abrupt voltage step at about 2.2 times the H_2/O_2 stoichiometric ratio. At low flow rates this voltage step occurs at stoichiometry. These findings are understood on the basis of mass transfer to a heterogeneous catalyst/electrode surface.

1. Introduction

Relatively few studies have been carried out on concentration cells exposed to non-equilibrium chemical mixtures. The present work is part of a larger research programme directed at such situations [1–5]. Specifically, we report substantial shifts in cell voltage–composition curves caused by changes in flow rate past the cell.

The experiment consisted of measuring the cell voltage developed across a ZrO_2 ceramic membrane with platinum catalyst/electrodes attached to each surface. When the gases are equilibrated the cell voltage is related to P_{O_2} and P'_{O_2}, the oxygen partial pressures on opposite sides of the membrane, by

$$V = \left(\frac{RT}{4F}\right) \ln \{P_{O_2}/P'_{O_2}\}. \tag{1}$$

The effective oxygen partial pressure and, consequently, cell voltage are ill-defined if non-equilibrium gas mixtures are used. When catalytic oxidation reactions occur on the electrode surfaces, cell voltage is influenced by (a) gas diffusion between the bulk gas and the electrode boundary layer; (b) rates of adsorption, desorption and surface reaction. Previous studies have considered these processes in situatons where the electrode surfaces could be viewed as homogeneous reaction zones [4, 5]. The present results are best interpreted via a heterogeneous reaction zone structure.

2. Experimental details

Oxygen sensors were constructed in this laboratory from tubes of ZrO_2 doped with 8 wt% Y_2O_3 (Zircoa Products). The tubes were closed at one end where platinum paste electrodes were attached to the inner and outer ZrO_2 surfaces. The inner reference electrode was exposed to air and the outer sampling electrode, to various gas mixtures. The sensing electrode had a surface area of 0.25 cm^2.

The sensor was housed in a quartz tube and located in a tube furnace. Furnace temperatures were monitored with a thermocouple. Gases of varying composition were mixed externally and travelled through a flow system past the sensor. In some experiments, a secondary catalyst (high surface area platinum supported on Al_2O_3) was used to equilibrate the gases before they reached the sensor. A three-way stopcock routed the gas stream by one of two paths: (a) over the secondary catalyst; or (b) directly to the sensor.

Reagent grade gases were used. Rotometers were used to control H_2, CO and N_2 flow rates in the

system. Oxygen flow rates were regulated with a Matheson Model 8240 Mass Flow Controller. This unit was modified electrically so that O_2 flow could be controlled by external voltage. Triangular waveforms from a Princeton Applied Research Model 175 Programmer were used to sweep oxygen concentrations. All data reported in this paper were obtained at 600° C with an O_2 flow rate variation of $\pm 4 \times 10^{-4}$ cm^3 s^{-2}, and at total flow rates of 13–70 cm^3 s^{-1}. Changing the oxygen concentration at slower sweep rates produced no variation in sensor voltage–sweep voltage curves, and the traces were identical for both increasing and decreasing O_2 partial pressure. Voltage–partial pressure traces made with O_2–N_2 mixtures at 600° C exhibited a close correspondence to Equation 1. For these reasons, the data are taken to represent steady-state results. Sensor voltage was amplified by a high impedance potentiostat and recorded on a Hewlett-Packard 7046A X–Y recorder.

3. Results and discussion

Experimental voltage–composition curves for (a) the H_2–O_2 and (b) the CO–O_2 systems are shown in Fig. 1. Compositions are expressed in the λ-notation [1, 2] where λ is the O_2/reactant partial pressure ratio divided by the corresponding ratio at stoichiometry. Measurements were made with and without gas pre-equilibration over the secondary catalyst. Within the accuracy of the O_2 Mass Flow Regulator, catalyst pre-equilibrated gases exhibited a voltage step at λ = 1.0. This was an expected consequence of the enormous change in equilibrium oxygen partial pressure which occurs at stoichiometry in these systems. In subsequent experiments the location of λ = 1.0 was determined from the voltage step with catalyst pre-equilibrated gases rather than from relative flow meter settings.

As shown in Figs 1 and 2, unequilibrated H_2–O_2 mixtures gave results that differ substantially from those obtained with pre-equilibrated H_2–O_2. A gradual voltage decline extending over the composition range $1 < \lambda < 4$ replaced the voltage step at λ = 1. The shape of the voltage–composition curves obtained with unequilibrated H_2–O_2 was sensitive to the total gas flow rate. Low flows gave a fairly sharp voltage step near λ = 1. With higher flow rates the voltage step broadened and moved towards λ = 4. Cederquist *et al.* [3] first reported unusual steady-state characteristics of ZrO_2 sensors towards H_2. This work was extended by Takeuchi *et al.* [4] who obtained definitive evidence of non-stoichiometric voltage steps in the H_2–O_2 and D_2–O_2 systems. Working with high flow rates at 400° C, they measured steps at λ = 4 in H_2–O_2 and at λ = 2 in D_2–O_2. Shifts of the voltage step away from λ = 1 were confirmed in later experiments by the present authors [5]. Takeuchi *et al.* [4] explained the origin of the shift via mass transfer arguments. Hydrogen diffuses faster than oxygen. Consequently, as both species are consumed in a surface chemical reaction, hydrogen from the exterior bulk gas can replenish the surface faster than bulk oxygen. This reasoning links the voltage to the molecular weights of the reactants, M_r and M_{O_2}. It predicts a voltage step at $\lambda = [M_{O_2}/M_r]^{1/2}$; i.e. at λ = 4 for H_2–O_2 and at λ = 2 for D_2–O_2.

It has been reported previously [4, 5] that the magnitude of experimental voltage-step shifts in the H_2–O_2 system is dependent on the total gas flow rate, but no explanation of the flow sensitivity has been given. It would appear that the flow dependence can be understood by combining mass transfer
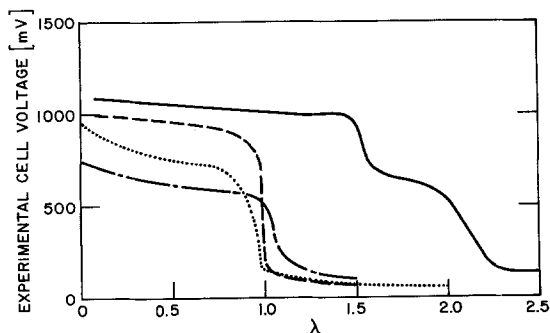

Fig. 1. Experimental sensor voltage–composition curves at 600° C. ——— 1% [V/V] H_2 in N_2 plus O_2 (unequilibrated); - - - - - 1% [V/V] H_2 in N_2 plus O_2 (pre-equilibrated); - - - - - 1% [V/V] CO in N_2 plus O_2 (unequilibrated); · · · · · 1% [V/V] CO in N_2 plus O_2 (pre-equilibrated).
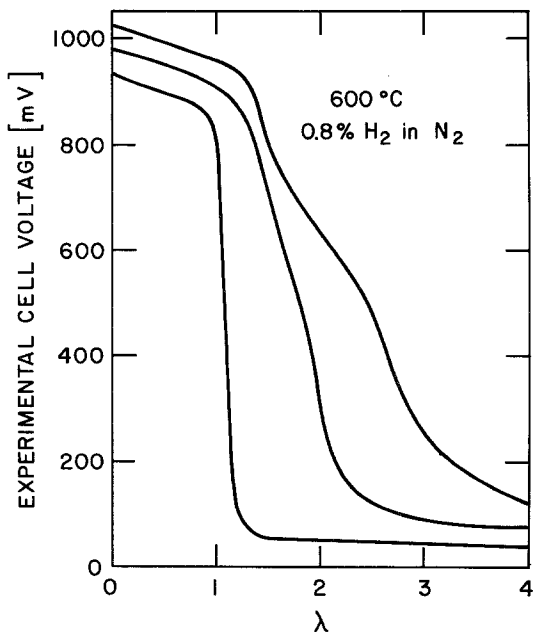
Fig. 2. Experimental sensor voltage—composition curves for unequilibrated H$_2$—O$_2$ mixtures at 600° C. Curves from left to right were obtained at total flow rates of 13, 33 and 70 cm^3 s^{-1}. All experiments used 1% [V/V] H$_2$ in N$_2$ and variable O$_2$ concentration.

arguments with a spatially varying bulk gas composition. This is conveniently formulated in terms of the schematic sensor/flow geometry shown in Fig. 3. Catalytic theory [6] leads to difference equations linking (a) steady-state oxygen and hydrogen partial pressures in the bulk gas, $O_2^b(j)$ and $H_2^b(j)$; (b) steady-state oxygen and hydrogen partial pressures in the boundary layer adjacent to the sensor surface, $O_2^s(j)$ and $H_2^s(j)$; (c) the bulk gas flow rate, Z; and (d) bulk gas/boundary layer mass transfer rates for oxygen and hydrogen, k_1 and k_2.

$$O = Z[O_2^b(j-1) - O_2^b(j)] - k_1 \{0.5[O_2^b(j-1) + O_2^b(j)] - O_2^s(j)\}$$

$$O = Z[H_2^b(j-1) - H_2^b(j)] - k_2 \{0.5[H_2^b(j-1) + H_2^b(j)] - H_2^s(j)\}$$

$$O = k_1 \{0.5[O_2^b(j-1) + O_2^b(j)] - O_2^s(j)\} - 0.5GH_2^s(j)[O_2^s(j)]^{1/2}$$

$$O = k_2 \{0.5[H_2^b(j-1) + H_2^b(j)] - H_2^s(j)\} - GH_2^s(j)[O_2^s(j)]^{1/2}.$$
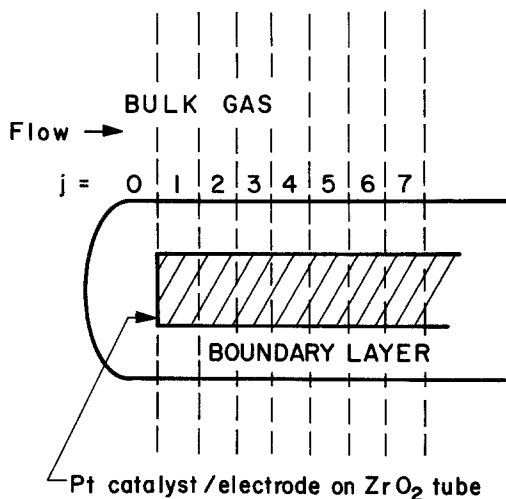

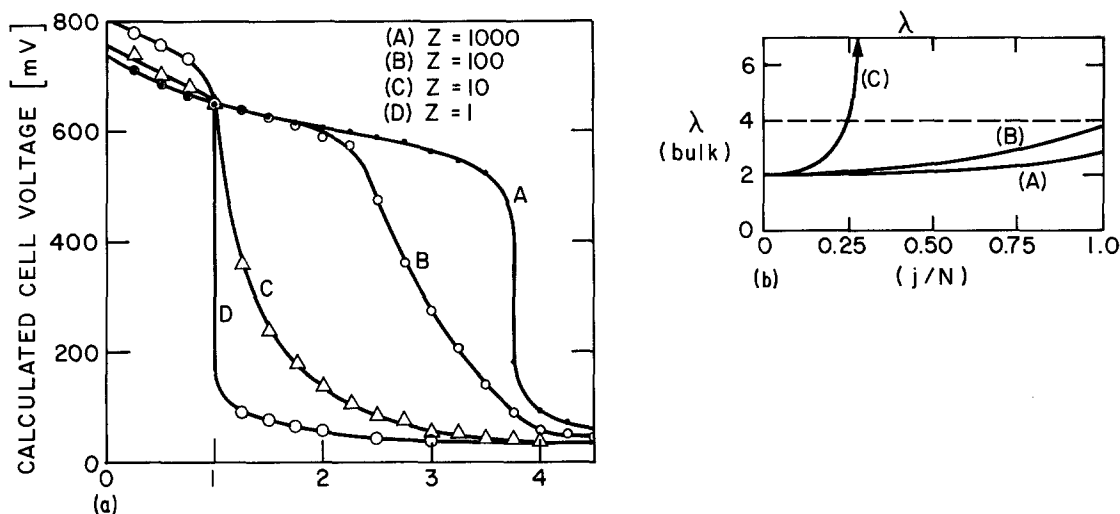Fig. 3. Schematic representation of sensor/flow geometry used in the kinetic model.

Fig. 4. Calculated sensor voltage–composition curves for (a) unequilibrated H_2–O_2. For all curves, $k_1 = 1$, $k_2 = 4$ and $G = 10^8$. The assumed flow rate, Z, is shown. (b) Calculated λ values in the bulk gas region as a function of fractional length along the sensor.

The index j runs from $j = 1$ at the end of the catalyst/electrode facing the incoming gas stream to $j = N$ at the other end. G is a surface rate constant for the $\frac{1}{2}O_2 + H_2$ reaction. These equations can be solved numerically assuming $H_2^b(0)$ and $O_2^b(0)$ are known input gas concentrations. Resulting boundary layer oxygen partial pressures can be used to calculate an average sensor voltage in either of two ways: (a) one can first average all $O_2^s(j)$ then apply Equation 1 to obtain a voltage; or (b) one can compute local voltages by applying Equation 1 to the $O_2^s(j)$, then average the results. Calculated voltage–composition curves from either method lead to qualitatively similar results. It should be noted that this use of Equation 1 presupposes that surface adsorption and desorption rates are fast compared to the rates of mass transfer and chemical reaction.

Results of numerical calculations (Fig. 4) and experiment (Fig. 2) are in fairly good agreement. Kinetic gas theory [6] predicts that mass transfer rates vary with $M^{-1/2}$. Consequently, $k_2/k_1 = 4$ was used in the calculations. The rate of surface reaction, $GH_2^s(j)O_2^s(j)^{1/2}$, was taken to be much faster than boundary layer/bulk gas mass transfer rates. This is consistent both with catalysis results [6] and with a previous analysis of ZrO_2 concentration cell voltage with non-equilibrium gas mixtures [5]. The numerical value used, $G = 10^8$, was arbitrary: any large number produced substantially identical results. Use of 7, 25 and 50 element spatial grids produced analogous variations of cell voltage with flow rate. The results obtained using the model indicate that flow sensitivity and voltage step broadening arise when the surface reaction at one location on the catalyst/electrode changes the downstream bulk gas composition. As shown in calculated composition distance profiles (bottom of Fig. 4) this leads to situations where part of the surface is in contact with a bulk gas containing excess H_2 while the remainder of the surface experiences a bulk gas with excess O_2. Because of the $k_2/k_1 = 4$ ratio, a large change in boundary layer oxygen occurs at $\lambda = 4$ rather than at $\lambda = 1$.

At high flow rates the entire surface effectively experiences the inlet H_2–O_2 composition and the voltage step occurs at $\lambda = 4$ as computed by earlier mass transfer arguments [3, 4]. At low flow rates the first section of the catalyst/electrode serves the same function as the external catalyst and equilibrates the H_2–O_2 bulk mixture. An equilibrium oxygen partial pressure is monitored at downstream sections of the electrode. Together, these downstream sections dominate the voltage averaging process. Consequently, the voltage step occurs at $\lambda = 1$.

The shoulder of the experimental ΔV–λ curves is not reproduced by the models. This may reflect details of the bulk gas/boundary layer mass transfer process that are not treated by the simplified kinetics used in the present model.

Acknowledgements

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