The transient start-up response of a universal exhaust gas oxygen sensor to investigate the Nernst equation in platinum/zirconia cells

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ABSTRACT

The universal exhaust gas oxygen sensor (UEGO) is a device used to infer the combustion air-to-fuel ratio of an internal combustion engine by sampling the exhaust gas. The sensor operates using a feedback system to maintain a specified internal condition, and measures the oxygen current required for this. While the steady state operation of the sensor is reasonably well-understood – dominated as it is by the diffusion of gas species – the factors influencing the transient response are not so clear.

In this paper a numerical model of a sensor is compared to experimental data. By examining the effect of the inclusion of different aspects into the model, it becomes clear that it is necessary to account for the influence of gaseous species adsorbing onto surfaces, as well as the more traditional approach based on oxygen partial pressure, to correctly capture the transient response of a sensor containing a Pt|YSZ|Pt cell.

1. Introduction

The universal exhaust gas oxygen (UEGO) sensor has become a commonplace as a method to determine the non-dimensional air-fuel ratio (λ) of IC engines, and may form a part of a feedback control system of the engine. Its usage has increased in order to help meet increasingly stringent emission regulations for both diesel and gasoline engines. A related sensor, the so-called 'HEGO' (Heated Exhaust Gas Oxygen) sensor – also known as a 'narrowband' or 'switch-type' – is of a simpler design, has been used for significantly longer, and is an essential component of most gasoline engines where emission regulations exist. This sensor gives a virtually binary output, depending upon whether the exhaust is a product of rich or lean combustion. However the UEGO, also known as a 'wideband' sensor, gives a measure of how rich or lean the combustion is. Under steady conditions the UEGO output is dominated by the diffusion of gases, and this aspect has been modelled previously [1].

Though designs vary considerably, the schematic of a common type is shown in Fig. 1 The key components of a UEGO are the 'reference cell', the 'pump cell', the measurement cavity, and the 'diffusion barrier' built mainly from layers of yttria-stablisedzirconia (YSZ). At elevated temperature YSZ is a good conductor of oxygen ions. The method of operation is based on achieving a constant oxygen partial pressure in the measurement cavity. The desired state is identified via the Nernst potential generated by the reference cell – if the potential is lower than the reference voltage (i.e. the oxygen partial pressure is too high), then the feedback circuit corrects this by causing the pump cell to extract more oxygen from the measurement cavity. The reverse happens if the reference cell potential is higher than the reference voltage. The pumped oxygen passes through the pump cell in the form of O^{2-} ions. The actual rate of oxygen pumping required is determined by the diffusion of gases through the diffusion barrier from the sample gas to the measurement cavity. Under rich exhaust conditions ($\lambda < 1$) an excess of hydrogen and carbon monoxide diffuse into the cavity, the oxygen required to oxidise these is produced by the breakdown of water and carbon dioxide on the side of the pump cell exposed to the sample gas and pumped into the cavity. Under lean exhaust conditions ($\lambda < 1$) oxygen gas diffuses through the diffusion barrier, and is pumped out of the cavity. The quantity of O^{2-} pumped is thus an indication of the leaness/richness of the sample gas. The sensor design considered here is the Bosch LSU4.2, further references to 'UEGO' refer to this type.

Though under steady conditions the UEGO response is determined by the diffusion barrier, under transient conditions this is not true. This is clearly seen in the sensor response to a sample gas crossing stoichiomtery [2]. In this case the Nernstian potential of the pump cell changes very rapidly, and the sensor output departs from the value predicted by gas diffusion through the barrier. To

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Simulation parameters

Nomenclature

T	temperature (K)
c_i	concentration of species i
p	pressure (Pa)
r	radial coordinate
X_i	mole fraction of species i
E	electrical potential
E	electric field
i	electrical current

Constants

$\Re$	molecular gas constant, $8314.41\,\mathrm{J\,kmol^{-1}\,K^{-1}}$
F	Faraday constant, $9.648 \times 10^7\,\mathrm{C\,kmol^{-1}}$
Γ	density of adsorption sites on Pt surface, $1.6603 \times 10^{-8}\,\mathrm{kmol\,m^{-2}}$ [12]
τ	diffusion barrier tortuosity, 1.5 [1]
d_p	diffusion barrier pore diameter, 1.85 μm [1]

Gas transport in the diffusion barrier [1]

$M_i\ (O_2 \to 32,\ N_2 \to 28)$ molecular mass of species i

$A_A = \left(\frac{1}{A_C} + \frac{1}{A_K} \right)^{-1}$ pressure drop coefficient

$D_{i,j} = \left(\frac{1}{D_{C_{i,j}}} + \frac{1}{D_{K_i}} \right)^{-1}$ diffusivity of species i in j

$A_C = \frac{\Re T}{p} \frac{32\mu}{d_p^2 \Sigma_i \left(X_i M_i^{0.5} \right)}$ continuum pressure drop

$A_K = \frac{3}{2d_p} \sqrt{\frac{\pi \Re T}{2}}$ free molecular pressure drop

$D_{C_{i,j}} = \frac{0.0101325 T^{1.75} \sqrt{1/M_i + 1/M_j}}{p \left(v_i^{1/3} + v_j^{1/3} \right)^2}$ continuum diffusivity

$D_{K_i} = \frac{d_p}{3} \sqrt{\frac{8\Re T}{\pi M_i}}$ free molecular 'diffusivity'

$Sc = 0.7$ Schmidt number for gas

$v_i\ (O_2 \to 16.3,\ N_2 \to 18.5)$ diffusion volume of species i [15]

Oxygen adsorption to the Pt surface in Eq. (8). [12]

θ fractional coverage of oxygen on Pt surface sites

$\mathcal{F}_{O_2} = \frac{p_{O_2}}{\sqrt{2\pi M_{O_2} \Re T}}$ molecular flux onto surface

$\zeta = 0.18 \exp\left(-14.1\theta \right)$ sticking probability

$k = 0.05 \exp\left(\frac{(4-5\theta) \times 10^6}{\Re T} \right)$ adsorbed molecular decomposition to desorption rate ratio

$k_d = 1.45 \times 10^{21} \exp\left(\frac{-(240 - 50\theta) \times 10^6}{\Re T} \right)$ adsorbed atomic oxygen desorption rate (m^2 kmol^{-1} s^{-1})

explore this further, this paper will focus on the transient response of the UEGO in ambient air, and examine the mechanism by which the voltage across the reference cell is generated.

2. Background theory

2.1. Pressure based Nernst equation

As discussed above, the feedback system within the UEGO which causes a flow of O^{2-} through the YSZ pump cell, is determined by the voltage across the reference cell. The feedback system is designed to maintain this reference voltage at 0.45 V, which corresponds to a stoichiometric gas mixture, i.e. $\lambda = 1$. The traditional mechanism for this voltage generation, as seen in [1,3,4], is considered to be purely a function of the partial pressures of oxygen in

the measurement cavity (cav) and reference gas (ref), the so-called Nernst potential.

$$E = \frac{\Re T}{4F} \ln \left(\frac{p_{O_2,\text{ref}}}{p_{O_2,\text{cav}}} \right) \tag{1}$$

Here $\Re$ is the universal molar gas constant, T the absolute temperature, F Faraday's constant, and p_{O_2} the partial pressure of oxygen. The factor of 4 arises from the fact that an oxygen molecule ionises to form two O^{2-}, therefore the negative charge associated with ionisation is 4. This equation is derived from the difference in entropy, S, between the two gas compositions, following the derivation found in [5] and beginning with Boltzmann's equation $S = k_B \ln \Omega$ (k_B being the Boltzmann constant). The number of states available Ω is considered inversely proportional to the pressure of the gas. The equation for Gibbs free energy G, noting that the enthalpy change across the reference cell (ΔH) is zero because the same species is being considered, can also be linked to the electromotive potential E of a reaction including the number of electrons involved z and the elementary charge e: $\Delta G = \Delta H - T\Delta S = -zeE$. Combining these we have

$$E = \frac{-T}{ze} \left(k_B \ln \left(\frac{1}{p_{O_2,\text{ref}}} \right) - k_B \ln \left(\frac{1}{p_{O_2,\text{cav}}} \right) \right) \tag{2}$$

Using the fact that in this case $z = 4$ and $k_B/e = \Re/F$ leads directly to Eq. (1) is reached. The reference voltage being set to 0.45 V and the reference gas being ambient air this leads to a conclusion that the partial pressure of oxygen within the measurement cavity is approximately 2.9×10^{-5} Pa.

2.2. Diffusion/drift based Nernst equation

Yttria-stablised-zirconia is a ceramic composed of the elements yttrium, zirconium, and oxygen. Yttrium and zirconium are transition metals of adjacent atomic number, meaning they are of similar atomic size but differing ionisation states. The similar size means yttrium can be inserted, or 'doped', into the lattice structure of zirconium oxide and the different stable ionic states lead to a vacancy in the lattice where an oxygen atom would normally sit. The vacancies are not restricted to remain next to the dopant ion as electrical neutrality is maintained wherever a vacancy lies. Oxygen conduction is achieved by O^{2-} swapping location within the lattice with a vacancy (denoted $V_O^{\circ\circ}$), and this ability for movement results in the possibility of diffusion if there is a gradient in the concentration of vacancies $[V_O^{\circ\circ}]$ or electrical drift should a voltage gradient act upon the ions. Vacancies can be considered to have a charge of +2, as although there is nothing present it is a location a 2− ion could sit, and in the analysis of [6] it is the vacancies that are examined.

Vacancy flux **J** due to diffusion is simply proportional to the diffusivity of vacancies $\mathcal{D}$ and the concentration gradient, $\mathbf{J}_{\text{diff}} = -\mathcal{D}\nabla[V_O^{\circ\circ}]$. The flux due to an applied electric field **E** is dependent on the field, the local concentration of vacancies to be effected, and the mobility μ_q of vacancies – a measure of the terminal velocity when an electric field acts on an ion. $\mathbf{J}_{\text{elec}} = \mu_q[V_O^{\circ\circ}]\mathbf{E}$

The Einstein–Smoluchowski relationship enables the two sources of vacancy flux to be combined, relating the mobility to diffusivity: $\mu_q = ze\mathcal{D}/k_BT$. That these values are related is no surprise as they are both measures of how ions (or vacancies in this case) move through a lattice. There is no current flow through the reference cell, so the combined diffusion and electrically driven fluxes must cancel.

$$0 = -\mathcal{D}\nabla[V_O^{\circ\circ}] + \mu_q[V_O^{\circ\circ}]\mathbf{E} \tag{3a}$$

$$\Rightarrow \mathcal{D}\nabla[V_O^{\circ\circ}] = \frac{ze\mathcal{D}}{k_BT}[V_O^{\circ\circ}]\mathbf{E} \tag{3b}$$