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Materials for high temperature electrochemical applications: Automotive sensors, catalysts and traps[☆]

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ABSTRACT

Extensive emissions and fuel economy directives are stimulating the development of every more sophisticated sensors, catalyst systems and emissions traps with improved performance and self-evaluation capabilities. For the development of such systems, deeper insights are required to understand the often complex interplay between the chemical state of the material and its electrical, optical, thermal and mechanical properties. Three examples, illustrating how information gained about the defect, electronic and transport structure of oxide materials can be used to optimize sensor and catalyst properties, are presented. Also discussed are means for in situ monitoring of the status of exhaust catalysts and traps.

1. Introduction

Automotive emissions controls have now been in place for over three decades, with great strides achieved in decreasing hydrocarbon, CO and NOx emission levels by the application of gas sensors and catalytic convertors [1]. The importance of this achievement cannot be overemphasized, given the number of internal combustion-engined vehicles operating worldwide, estimated to be 800 million, consuming over 200 billion US gallons of gas or diesel annually [2]. The drive towards improved fuel efficiency has stimulated the development of various lean burn engine technologies with resultant needs for alternative sensors, gas catalysts and traps. For these systems, deeper insights are required to understand the often-complex interplay between the chemical state of the material and its electrical, optical, thermal and mechanical properties.

A schematic of an automotive exhaust system, including key emissions control features, is shown in Fig. 1. In today's engines, the 3-way catalyst is essential for removing the large majority of unburned hydrocarbons, CO and NOx in the exhaust gas, with the assistance of the potentiometric O_2 sensor operating in feedback mode (sensor 1) [3]. Other sensors are sometimes placed at the exit of the catalyst/trap to monitor the overall efficacy of the system (sensor 2) [4]. Means of sensing the actual state of a catalyst/trap would alert the system to when it needs to be refreshed, recalibrated or replaced (sensor 3) [5]. Examples of each type of sensor are examined, illustrating how information gained about the defect, electronic and transport structure of oxide materials can be used to optimize sensor and catalyst/trap properties.

2. Self-temperature compensated oxygen sensor

The standard potentiometric oxygen exhaust sensor utilizes a stabilized zirconia ceramic electrolyte with catalytic platinum electrodes, generating a Nernst potential related to the air to fuel (A/F) ratio in the exhaust given by

$$E_{\text{Nernst}} = \frac{kT}{4q} \ln \left(\frac{pO_2}{pO_2^{\text{ref}}} \right) \quad (1)$$

in which pO_2 is the oxygen partial pressure of the exhaust gas, pO_2^{ref} that of the reference, typically air, k is the Boltzmann constant, T is the sensor temperature in K and q is the charge of the electron.

This sensor works well when exposed to near stoichiometric A/F ratios, where it detects shifts in pO_2 of many orders of magnitude, as the exhaust gas transitions from rich to lean burn conditions. The output of the sensor is used in feedback manner to maintain the appropriate A/F ratio for optimum operation of the 3-way catalyst [3]. For lean burn engines, the logarithmic dependence of EMF on pO_2 is too weak to work reliably. An attractive alternative is the use of pO_2 sensitive oxide semiconductors, such as $SrTiO_3$, for which the electrical conductivity follows a power law dependence on pO_2 of the type [6]

$$\sigma \propto pO_2^m \exp \left(\frac{-E_0}{kT} \right) \quad (2)$$

Besides higher sensitivity, such resistive sensors offer low cost fabrication, potential for miniaturization and no need for seals and

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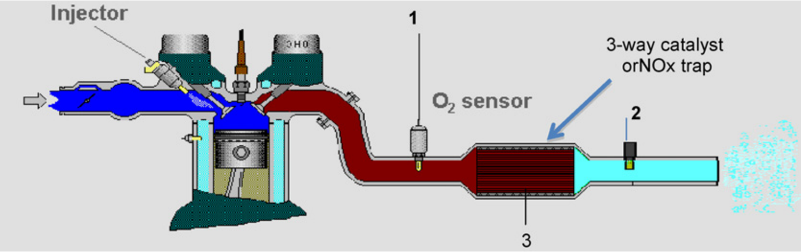

Fig. 1. Exhaust system schematic showing three types of sensors. Sensor 1 – monitors gases in exhaust; sensor 2 – monitors gases leaving catalyst/trap; sensor 3 – monitors state of catalyst/trap.

Image: courtesy of W. Menesklou.

reference atmospheres, as required by zirconia-based sensors. A major limitation, however, is the significant cross sensitivity to temperature variations via the material's exponential dependence on temperature (see Eq. (2); large E_O). Based on a defect chemical analysis, the measured value of E_O corresponds to the oxidation reaction [2]

$$\tfrac{1}{2}O_2 + V_O^{\bullet\bullet} \Leftrightarrow O_O^x + 2h^{\bullet} \qquad (3)$$

$$K_O = p^2[V_O^{\bullet\bullet}]^{-1}pO_2^{-(1/2)} = k_O \exp\left(\frac{-E_O}{kT}\right) \qquad (4)$$

in which $V_O^{\bullet\bullet}$ is a doubly ionized oxygen vacancy, $h^{\bullet}$ an electron hole, p their concentration and K_O the equilibrium constant of the reaction. For $SrTiO_3$, E_O = 1.3 eV which would result in ∼2% change in resistance per °C, equivalent to an ∼8% change in pO_2 [7]. This temperature cross sensitivity renders $SrTiO_3$, and most other semiconducting oxides, unsuitable for this purpose.

A solid solution between strontium titanate and ferrite, given by $Sr(Ti_{0.65}Fe_{0.35})O_{3-\delta}$ (STF35), on the other hand, has been found to exhibit a near zero temperature coefficient of resistance [7]. Indeed even higher Fe concentrations actually result in a positive coefficient of resistance (PTCR), contrary to that expected for semiconducting oxides. An explanation of these unusual results requires an understanding of the interplay of the material's defect chemistry, transport properties and electronic band structure. Briefly, the introduction of Fe into the lattice initially creates discrete acceptor levels within the band gap, contributing to the p-type nature of STF in air. With increasing Fe, these levels broaden into a band that begins to overlap the O 2p derived valence band, leading to a decrease in band gap energy from ∼3.3 eV to ∼2.7 eV for the above STF35 composition [8]. The p-type conductivity, including all the temperature dependent components, can be written as [9]

$$\sigma = \sigma_0 T^{(1.5-m)} \exp\left(\frac{-E_F}{kT}\right) \qquad (5)$$

where m reflects the power law dependence of mobility on temperature and E_F is the Fermi energy measured relative to the top of the valence band. Applying the definition of TCR to Eq. (5) yields

$$\mathrm{TCR} = \frac{1}{R}\frac{dR}{dT} = \frac{m}{T} - \frac{3/2 + E_F/k_T}{T} \qquad (6)$$

Normally the first term in Eq. (6), which contributes to PTCR, is overwhelmed by the second term, largely deriving from the exponential term in Eq. (5), leading to a negative temperature coefficient of resistance (NTCR). However, with the reduced band gap, the NTCR term becomes comparable to that of the PTCR term in Eq. (5), leading to a temperature insensitive oxygen sensor operation. The relative PTCR and NTCR contributions are indicated schematically in Fig. 2 by the size of the arrows adjacent to the respective terms TCR(μ) and TCR(p). While the TCR(μ) term is largely independent of pO_2, TCR(p) decreases with increasing pO_2. This can be understood from an examination of Eq. (4). The vacancy concentration in STF is largely fixed by the Fe concentration, which under the conditions of interest has an oxidation state of +3. Thus, as a first approximation, one can fix the vacancy concentration to:

$$[Fe'_{Ti}] = 2[V_O^{\bullet\bullet}] \qquad (7)$$

Substituting Eq. (7) into (4), one obtains a solution for the hole concentration given by

$$p = (1/2[Fe'_{Ti}]K_O)^{1/2}pO_2^{1/4} \qquad (8)$$

which shows the hole concentration increasing with increasing pO_2. Next considering the relationship between the hole concentration and the Fermi energy E_F, assuming non-degenerate statistics,

$$p = N_V \exp\left(\frac{-E_F}{k_T}\right) \qquad (9)$$

in which N_V is the effective density of states in the valence band, it becomes evident that the Fermi energy decreases with increasing pO_2 as:

$$E_F \propto -\tfrac{1}{4}\ln\ pO_2 \qquad (10)$$

as illustrated in Fig. 2. As a consequence, it is important to select the appropriate temperature and pO_2 range for which the value of E_F is sufficiently close to the top of the valence band to enable compensation of the PTCR effect connected with mobility, i.e., when the upward and downward pointing arrows in Fig. 2 become equal in magnitude. The results of numerical computations predicting the range of pO_2 and temperature for which the TCR remains below ∼0.4%/K are illustrated in Fig. 3. Here we see that near zero TCR can be achieved, in principle with $Sr(Ti_{0.65}Fe_{0.35})O_{3-\delta}$, in the pO_2 range of interest for lean burn conditions over the temperature range of ∼400–1000 °C.

In addition to temperature sensitivity, for the oxygen sensor to be able to provide adequate feedback to the engine control unit, it must respond quickly (typically 10 ms) to changes in pO_2. For this to be possible, diffusion times given by $\tau_{\tilde{D}} \propto l^2/\tilde{D}$ must be exceptionally low, where $\tilde{D}$ is the chemical diffusivity and l the diffusion

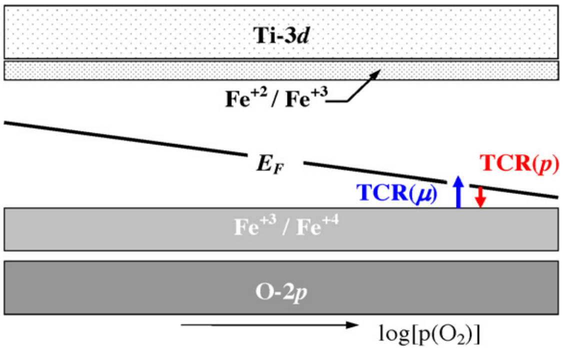

Fig. 2. The Fe derived band moves E_F close to the top of the valence band, markedly reducing the NTCR component of the resistivity of STF.

From Ref. [9].

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