A first-principles model of the zirconia oxygen sensor

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Abstract

Zirconia oxygen sensors are used extensively to monitor the air-to-fuel ratio of internal combustion engines. The basic physical and chemical processes involved in the sensing operation have been examined in detail to develop a first-principles model whose results agree well with experiments. Additionally, a wide variety of response is predicted from the model, depending upon the gas mixture, the electrode material, the reactivities of the gases, etc. The analysis is helpful in providing insight and design guidance in optimizing sensor operation for specific applications. © 1997 Elsevier Science S.A.

Keywords: Chemical sensor; Oxygen sensor; Zirconia sensor

1. Introduction

The zirconia oxygen sensor, commonly used for control of the air-to-fuel ratio of internal combustion engines, consists of a thimble shaped non-porous oxygen-ion-conducting electrolyte (yttrium-stabilized zirconia) which separates the reference gas (e.g. air) from the measurement gas (e.g. exhaust gas from an internal combustion engine). A heater is provided to control the temperature and, under open circuit conditions, an e.m.f. develops between the porous outer (measurement) and inner (reference) Pt electrodes. When the system is in thermodynamic equilibrium, the sensor senses only the oxygen partial pressure in the measurement gas. The exhaust gas from an internal combustion engine, however, is not in thermodynamic equilibrium and the sensor e.m.f. depends upon the partial pressures of the constituent gases and other factors. Experimental and theoretical studies of the sensor response in different measurement gas environments are therefore necessary for an understanding of the sensor behavior and for optimal use of the device in various applications.

In the laboratory studies, one uses measurement gases of known composition [1] to determine the sensor response. Such studies are also easy to compare with the predictions of theoretical models. Early models [2–4] of zirconia oxygen sensors had only limited success. In recent publications [5–7], a first-principles model of the operation of electrical-type metal oxide gas sensors was developed and used to analyze the response of electrochemical and resistive gas sensors to simple gas mixtures containing oxygen and one reducing (combustible) species. Subsequently, preliminary results on modeling the response of zirconia (ZrO_2) sensors to more complex gas systems comprising oxygen and a mixture of reducing gases were presented [8,9]. In this paper, some more results for one reducing gas case are given, the model for two reducing-gas mixtures is described in detail and the results are compared with experiments.

2. The model

When the measurement electrode of a zirconia oxygen sensor is exposed to a gas mixture, the gas molecules reaching this electrode are adsorbed and react in various ways, and the products desorb and sometimes react among themselves. Such processes involving oxygen and the reducing species affect the oxygen adatom concentration on the sensor electrode which in turn changes the charged oxygen vacancy concentrations inside the solid electrolyte (zirconia). The difference in charge density in the material near the

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two electrodes, along with the electronic charge on the electrodes, gives rise to the observed sensor e.m.f. The chemical part of the sensor model [6,7] involves equations describing the transport of the gas molecules to and away from the solid surface (by diffusion or flow) and the rates of change of the surface concentrations of various species due to adsorption, desorption, and reaction on the solid surface (e.g. electrode).

The electrical part of the sensor derives from the electrostatic field generated by charged oxygen vacancies inside the zirconia electrolyte and electrons in the electrodes. In the simplest case, the coupling between the chemical and the electrical parts of the sensor is through the electrochemical reaction of an adsorbed oxygen atom, an oxygen vacancy in the zirconia, and electrons in the electrode:

$$O_{ads} + v_O^{2+} + 2e^- \text{(electrode)} \leftrightarrow O_O \qquad (1)$$
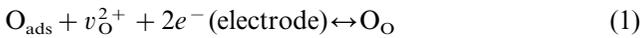
where v_O^{2+} represents the doubly charged oxygen vacancy and O_O is an oxygen atom of the oxide. In more complex cases, additional electrochemical reactions involving adsorbed reducing species, M, may occur, e.g.

$$M_{ads} + O_O \leftrightarrow MO_{ads} + v_O^{2+} + 2e^- \text{(electrode)} \qquad (2)$$
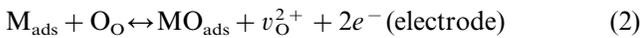
Such processes change the charge density inside the solid electrolyte close to the electrodes. The solution of the electrostatic potential problem provides an expression for the e.m.f. generated across the electrochemical zirconia cell in terms of the concentration of the adsorbed oxygen. The latter can be obtained from the solution of the equations describing the chemical mechanisms operative in the sensor. In this paper, only the electrochemical reaction given by Eq. (1) will be included; the results of including the additional electrochemical reaction given by Eq. (2) has already been reported in another publication [10].
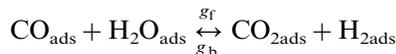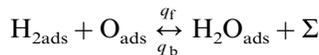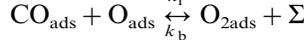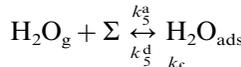
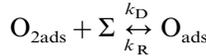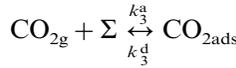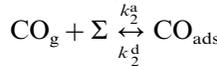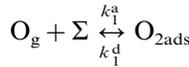The basic equations of the model for the one-reducing gas case has been described in previous [6,7] publications. A gas mixture like O_2–CO–CO_2, with one reducing gas CO, is characterized by the so-called inverse redox ratio R' ($= 2p_{O_2}/p_{CO}$), defined in terms of the partial pressures p_{O_2}, p_{CO} in the measurement gas far away from the electrode. The model [6,7] leads to a polynomial equation for the oxygen adatom concentration θ_O on the electrode surface (or for a variable z which is proportional to θ_O and which obviously depends upon the gas-mixture composition R'). Solution of this equation may be used [6,7] to predict the sensor e.m.f. as a function of R' at the given absolute temperature T. The sensor e.m.f. (in millivolts) is given by

$$V_O = (T/46.42)[\ln(p_{air}/p_{O_2}) - 2\ln(z(R'))] \qquad (3)$$

If the measuring electrode is highly catalytic (large k_f, see below) and near thermodynamic equilibrium prevails locally at the electrode (in which case $z(R') = 1$ for all R'), then the sensor e.m.f. is defined essentially by

the equilibrium oxygen partial pressure and shows a stepwise change from a high to a low value at the stoichiometric gas composition which corresponds to $R' = 1$. In the absence of thermodynamic equilibrium, the response of the sensor varies widely depending on the properties of the electrode material. For example, the position of the step ('switch-point') may be shifted to values smaller or larger than $R' = 1$ (stoichiometry). Also the high e.m.f. may be large or small, leading to different step sizes.

The extension [8,9] of the model to the case of the zirconia sensor exposed to O_2–CO–CO_2–H_2–H_2O gas mixtures containing two reducing gases, CO and H_2, involves more complicated equations which are solved to compute the sensor e.m.f. The so-called inverse redox ratio, in this case, is given by $R' = 2p_{O_2}/(p_{CO} + p_{H_2})$, defined in terms of the partial pressures p_{O_2}, p_{CO} and p_{H_2}. The reactions on the electrode (whose vacant surface sites are denoted by Σ) may be written as follows:

$$O_g + \Sigma \underset{k_1^d}{\overset{k_1^a}{\leftrightarrow}} O_{2ads}$$

$$CO_g + \Sigma \underset{k_2^d}{\overset{k_2^a}{\leftrightarrow}} CO_{ads}$$

$$CO_{2g} + \Sigma \underset{k_3^d}{\overset{k_3^a}{\leftrightarrow}} CO_{2ads}$$

$$O_{2ads} + \Sigma \underset{k_R}{\overset{k_D}{\leftrightarrow}} O_{ads}$$

$$H_{2g} + \Sigma \underset{k_4^d}{\overset{k_4^a}{\leftrightarrow}} H_{2ads}$$

$$H_2O_g + \Sigma \underset{k_5^d}{\overset{k_5^a}{\leftrightarrow}} H_2O_{ads}$$

$$CO_{ads} + O_{ads} \underset{k_b}{\overset{k_f}{\leftrightarrow}} O_{2ads} + \Sigma$$

$$H_{2ads} + O_{ads} \underset{q_b}{\overset{q_f}{\leftrightarrow}} H_2O_{ads} + \Sigma$$

$$CO_{ads} + H_2O_{ads} \underset{g_b}{\overset{g_f}{\leftrightarrow}} CO_{2ads} + H_{2ads}$$
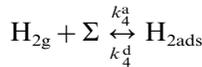
The concentrations of the species O_{ads}, O_{2ads}, CO_{ads}, CO_{2ads}, H_{2ads} and H_2O_{ads} on the surface of the electrode are denoted by θ_α, where $\alpha = 0, 1, 2, 3, 4$ and 5, respectively. Let the number of sites on the electrode surface accessible to all the adsorbed species be ω per unit area and let (dn_α/dt) be the rate of change of the number of particles of the species α. This change, due to the adsorption/desorption described above, can be written as:

$$(dn_\alpha/dt)/\omega = k_\alpha^a p_\alpha^{(0)} \theta_\alpha - k_\alpha^d \theta_\alpha \qquad (4)$$

where $p_\alpha^{(0)}$ are partial pressures at the electrode as opposed to the partial pressures p_α far away from the electrodes. Since mass transport of the gases to the electrode is responsible for the pressure difference, one can also write (note that $p_1 = p_{CO_2}$; $p_2 = p_{CO}$ etc.):

$$(dn_\alpha/dt)/\omega = D_\alpha(p_\alpha^{(0)} - p_\alpha)/(\kappa/D_1) \qquad (5)$$

where D_α are the diffusion coefficients, and the mass transfer coefficient κ depends upon temperature and detailed characteristics of the diffusional transfer of molecules from the bulk of the gas to the surface of the electrode. In the steady state, the coupled equations satisfied by θ_α are as follows:

$$(d\theta_1/dt) = 0 = (dn_1/dt)/\omega - k_D\theta_1 + (1/2)k_R\theta_0^2$$

$$(d\theta_2/dt) = 0 = (dn_2/dt)/\omega - k_f\theta_0\theta_2 + k_b\theta_3 - g_f\theta_2\theta_5$$
$$+ g_b\theta_3\theta_4$$

$$(d\theta_3/dt) = 0 = (dn_3/dt)/\omega + k_f\theta_0\theta_2 - k_b\theta_3 + g_f\theta_2\theta_5$$
$$- g_b\theta_3\theta_4$$

$$(d\theta_4/dt) = 0 = (dn_4/dt)/\omega - q_f\theta_0\theta_4 + q_b\theta_5 - g_f\theta_2\theta_5$$
$$+ g_b\theta_3\theta_4$$

$$(d\theta_5/dt) = 0 = (dn_5/dt)/\omega + q_f\theta_0\theta_4 - q_b\theta_5 + g_f\theta_2\theta_5$$
$$- g_b\theta_3\theta_4$$

$$(d\theta_0/dt) = 0$$
$$= 2k_D\theta_1 - k_R\theta_0^2 - k_f\theta_0\theta_2 + k_b\theta_3 - q_f\theta_0\theta_4 + q_b\theta_5$$
$$\tag{6}$$

Using the algebraic procedure described in the earlier work [6–9], it can be shown that the above equations can be cast into a single polynomial equation satisfied by a variable z which is directly proportional to θ_0:

$$\sum c_n z^n = 0 \tag{7}$$

where c_n are functions of the partial pressures (and hence R') and the rate constants defined above. This equation is solved for $z(R')$ which is used in Eq. (3) to compute the sensor e.m.f.

3. Results for one-reducing-gas mixtures

For given T and partial pressures, the computation of the sensor e.m.f. proceeds by assuming values of the rates of diffusion, adsorption, desorption and reactions. However, in the case of one-reducing-gas mixtures, these rates appear in specific combinations to yield two overall independent parameters: ξ, which determines the high e.m.f., and R'_s, which is the value of R' at the switch-point. For the O_2–CO–CO_2 gas mixture, one can express ξ and R'_s as follows:

$$\xi = [1 + (1 + k_1^d/k_D)\kappa/k_1^a]/[D_1/D_3 + (1 + k_3^d/k_b)\kappa/k_3^a] \tag{8}$$

$$R'_s = [1 + (1 + k_1^d/k_D)\kappa/k_1^a]/[(D_1/D_2) + (\kappa/k_2^a)] \tag{9}$$

A detailed comparison of this approach with the results of laboratory experiments will be reported in a forthcoming publication [10].
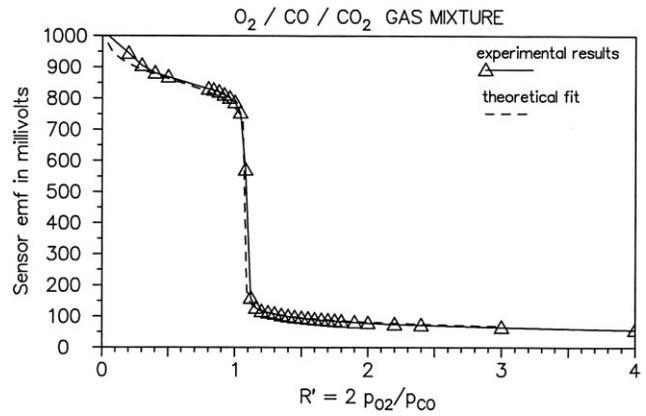

Fig. 1. Measured and model sensor e.m.f. at 837 K for O_2–CO–CO_2 gas mixture.

Fig. 1 shows the experimental result at a high temperature ($T = 837$ K corresponding to 564°C; similar results are obtained at higher temperatures) for a sensor exposed to O_2–CO–CO_2 gas mixture. The values of the rate constants were varied to obtain good theoretical fit. Similar result in the case of O_2–H_2–H_2O gas mixture is shown in Fig. 2, but the observed switch-point is not as sharp as the one predicted by the model. At a low temperature shown in Fig. 3 ($T = 631$ K corresponding to 358°C; similar results are obtained at lower temperatures), the low e.m.f. (at large values of R') predicted by the model is quite small in comparison with the experimental results. The agreement of the model prediction with experimental results improves significantly if the additional electrochemical reaction of Eq. (2) is included in the model as described in another publication [11].

The model may be used to predict changes in the sensor response as the electrode surface characteristics are changed. For example, the switch-point shifts if the rate of CO adsorption changes relative to that of O_2 as in Fig. 4 (for some values of the ratio k_2^a/k_1^a). These curves were obtained by changing appropriate rate
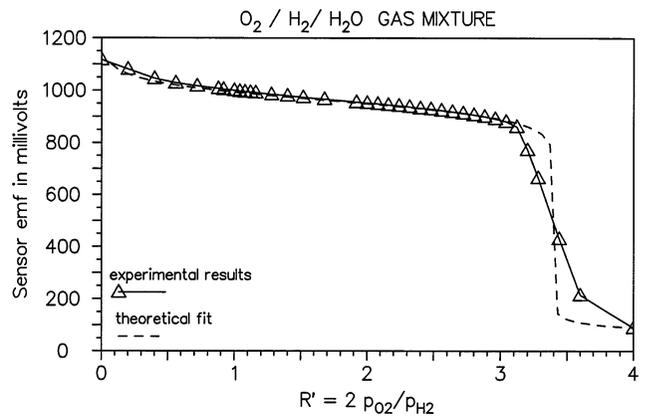

Fig. 2. Measured and model sensor e.m.f. at 837 K for O_2–H_2–H_2O gas mixture.
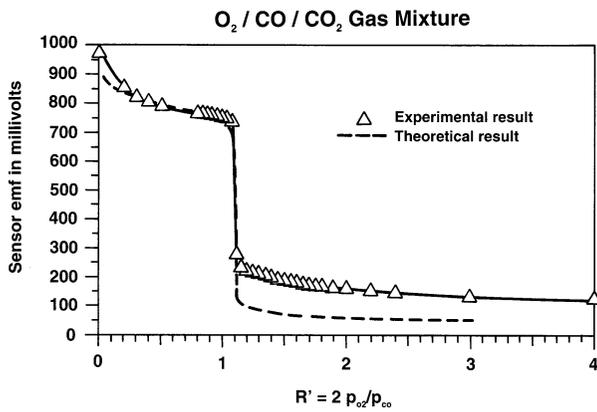
Fig. 3. Measured and model sensor e.m.f. at 631 K for O_2–CO–CO_2 gas mixture.

constants in the expressions for the parameters ξ and R_s'. Similarly, Fig. 5 depicts the effect of the rate of reaction, k_f, on the high e.m.f. (at small values of R'). It implies that more catalytic electrodes (larger reaction rate k_f) produce larger values of the high sensor e.m.f.

4. Results for two reducing gases: first version

The model for O_2–CO–CO_2–H_2–H_2O gas mixture has been developed in two versions. In the first version, we assume that CO and H_2 react with oxygen independently on the electrode surface and that the products, CO_2 and H_2O, do not react with anything. This corresponds to setting $g_f = 0$ in the reaction scheme described above. The second version of the model allows for the additional reaction of adsorbed CO with adsorbed H_2O, the so-called 'water–gas reaction', (non-zero g_f) as discussed in the next section. When $g_f = 0$, the equation satisfied by z (which is proportional to the oxygen adatom concentration on the electrode) is fourth order. Its solution allows the computation of the
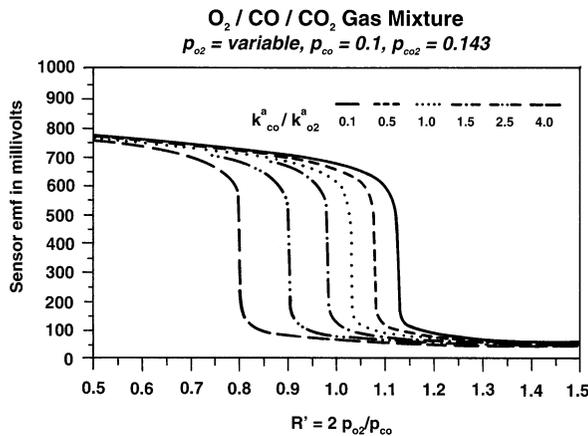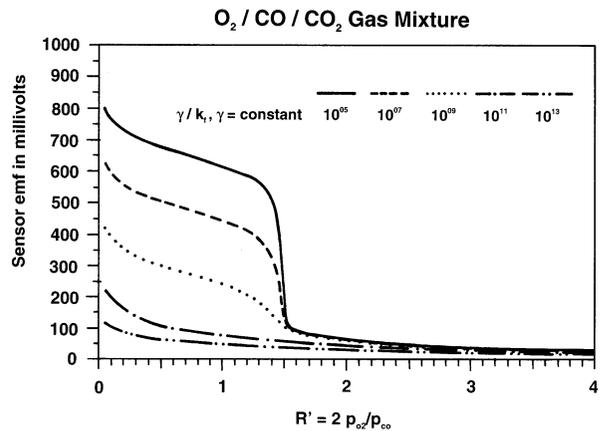

Fig. 5. Plots of e.m.f. versus R' for different reaction rates k_f, O_2–CO–CO_2 gas mixture.

sensor e.m.f. using Eq. (3).

If thermodynamic equilibrium is established at the electrode and diffusion effects are minimal, then the step is at the stoichiometric $O_2/(CO + H_2)$ ratio (similar to the case of a single reducing gas mixture). Otherwise, the response of the sensor varies widely. Even in thermodynamic equilibrium, diffusion effects of hydrogen will shift the step from stoichiometry. For gas mixtures not in thermodynamic equilibrium, there may be a single step or a double step (see below) in the e.m.f. as a function of the inverse redox ratio R' ($= 2p_{O_2}/[p_{CO} + p_{H_2}]$). The position of the step may shift from stoichiometry ($R' = 1$), and different step sizes are possible.

In comparing the model with the experimental results, first the model parameters were found separately for O_2–CO–CO_2 and O_2–H_2–H_2O gas mixtures by fitting the one-reducing-gas model to laboratory results for each of these gas systems. Using these parameters, the response of the sensor can be predicted for the two-reducing-gas mixture O_2–CO–CO_2–H_2–H_2O without introducing any other parameter provided that no water–gas reaction takes place. At high temperatures, the e.m.f. predicted in this way agrees very well
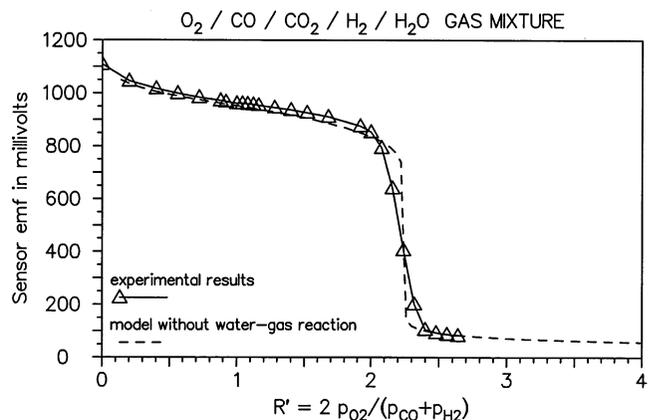

Fig. 4. Plots of e.m.f. versus R' for various rates of CO adsorption, O_2–CO–CO_2 gas mixture.

Fig. 6. Measured and model e.m.f. at 837 K, O_2–CO–CO_2–H_2–H_2O gas mixture.

Fig. 7. Measured and model e.m.f. at 631 K, O_2–CO–CO_2–H_2–H_2O gas mixture.
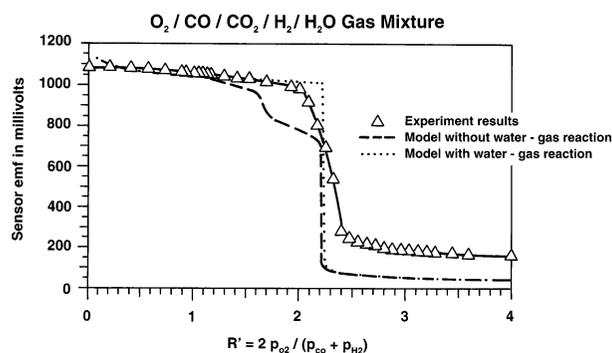

Fig. 8. Measured and model e.m.f. at 837 K, O_2–CO–CO_2–H_2–H_2O gas mixture.

with the experimentally observed e.m.f. as shown in Fig. 6 (where the temperature $T = 837$ K corresponds to 564°C and similar results are found at higher temperatures). At low temperatures, this first version of the model (i.e. without water–gas reaction) gives rise to two steps in the e.m.f. vesus R' curves as shown in Fig. 7 (where the temperature $T = 631$ K corresponds to 358°C; similar results are found at lower temperatures). However, such double steps are not observed experimentally. Analysis of the model equations shows that double steps will appear whenever the adsorption and reaction rates of the two reducing gases are different. The first step at the lower R' is associated with the reducing species which has the higher reaction rate. The position of the first step is determined by the adsorption rate of this reducing species, scaled by the fraction of reducing gas partial pressures. The second step is associated with the species which has the lower reaction rate and the position of this second step obeys the Rule of Mixtures [8,9].

5. Results for two reducing gases: second version

The second version of the model allows for the additional reaction of adsorbed CO with adsorbed H_2O (the so-called 'water–gas reaction'). This leads to a sixth-order equation for the oxygen adatom concentration. This more realistic case is treated quantitatively assuming suitable values of the water–gas reaction rate constant. Fig. 7 depicts the results obtained at a low temperature ($T = 631$ K, corresponding to 358°C). When the water–gas reaction is sufficiently strong, the double step behavior exhibited by the first version of the model at this low temperature (broken curve in Fig. 7) changes to a single step behavior (dotted curve). In this case, the water–gas reaction plays a crucial role in improving agreement with experiment by eliminating the double step. However, if the water–gas reaction is included at high temperatures, the result shown as the dotted curve in Fig. 8 ($T = 837$ K, corresponds to 564°C) is obtained. Clearly, the assumption of water–gas reaction is not particularly important in this case.
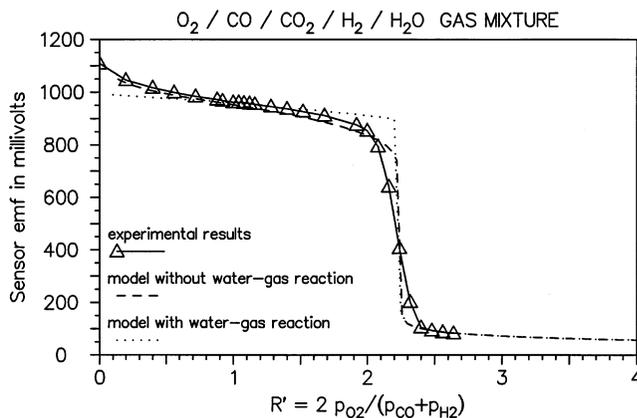
6. Conclusions

The model, based upon basic physics and chemistry, is a useful tool for understanding the effects of the various physicochemical processes involved in the operation of electrochemical sensors. It can also provide guidance in optimizing sensor performance for specific applications by suggesting suitable structural and materials modifications.

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Biographies

Alan Brailsford received his B.Sc., Ph.D. and D.Sc. degrees in mathematical physics from the University of Birmingham in 1953, 1956 and 1991, respectively. Dr Brailsford has worked upon problems in the electron theory of metals, dislocation dynamics, radiation effects in metals and alloys, and various topics in device physics. He is a Fellow of the American Physical Society, ASM and of the Institute of Physics. He has recently retired as the manager of the Physics Department of the Ford Research Laboratory.

Mohammed Yussouff received his M.Sc. in 1963 from Delhi University and his Ph.D. in 1967 from the Indian Institute of Technology, Kanpur, where he was Professor of Physics until 1991. He worked in Juelich and Konstanz as a Fellow of the Alexander von Humboldt Foundation. He is currently Visiting Professor at the Michigan State University and does research in the Physics Department of the Ford Research Laboratory. He has worked on channeling of ions, clusters, disordered systems, electronic structure of impurities in metals, foundations of quantum theory, ionic conductors, point defects, model of chemical sensors and the theory of freezing.

Eleftherios M. Logothetis received his B.S. degree in physics from the University of Athens, Greece, in 1959 and his M.S. and Ph.D. degrees in solid state physics from Cornell University in 1965 and 1967, respectively. He has been with Ford Motor Company since 1967 and he is currently senior staff scientist in the Ford Research Laboratory. He is a Fellow of the American Physical Society. His main research has been in the preparation and the electrical and optical properties of materials, solid state devices, in particular, chemical sensors.