

Electrochemical Sensors for Energy and Transportation

by Rangachary Mukundan and Fernando Garzon

Electrochemical sensors have widespread application in the automotive and energy industries—two major users of fossil fuels. The combustion of fossil fuels is a major source of air pollution and has been under increasing scrutiny by public and government organizations. Knowledge of the composition of emission gases is critical in optimizing process control parameters such as fuel/air stoichiometry and combustion temperature via feedback control. Solid-state and optical sensors are currently being used to analyze the gases of a combustion reaction thus enabling feedback control of the reaction. Although, this has greatly helped improve energy efficiency and reduce pollution, new and improved sensors are required to meet more stringent efficiency and pollution standards that will be mandated by various government agencies. This article discusses the current state-of-the-art solid-state sensor technology that is used in the automotive and energy industries for combustion control and details several promising technologies that are potentially useful to these two industries.

The most widely used electrochemical sensor is the oxygen sensor, which is used for automotive engine and boiler control. There are also several other electrochemical and semiconductor-type sensors that are commercially marketed to sense various gases like carbon monoxide (CO), hydrocarbons (HCs), nitrogen oxides (NO_x), sulfur oxides (SO_x), and volatile organic compounds (VOCs) in the atmosphere. However, these sensors have not found widespread use in the hostile environments encountered in the outlet streams of boilers and automotive engines. In this article we first discuss the various types of oxygen sensors that are currently in use and then describe the other electrochemical sensors that are being used to sense the presence of various combustible and/or toxic gases in the atmosphere. Finally we discuss the technologies

that have the potential for use in combustion control for NO_x , HC, and CO detection.

Oxygen Sensors

Oxygen sensors for automotive use were first introduced by Bosch in 1976 and have been standard on all passenger cars sold in the U.S. since 1980-

1981.¹ The oxygen sensor is used to control the air/fuel (A/F) ratio that is fed to the engine and, in combination with a three-way catalyst, has led to a dramatic reduction in pollution emissions from automobiles.² This sensor, also known as the heated exhaust gas oxygen (HEGO) sensor or λ -sensor, is a simple potentiometric electrochemical device that generates an electric poten-

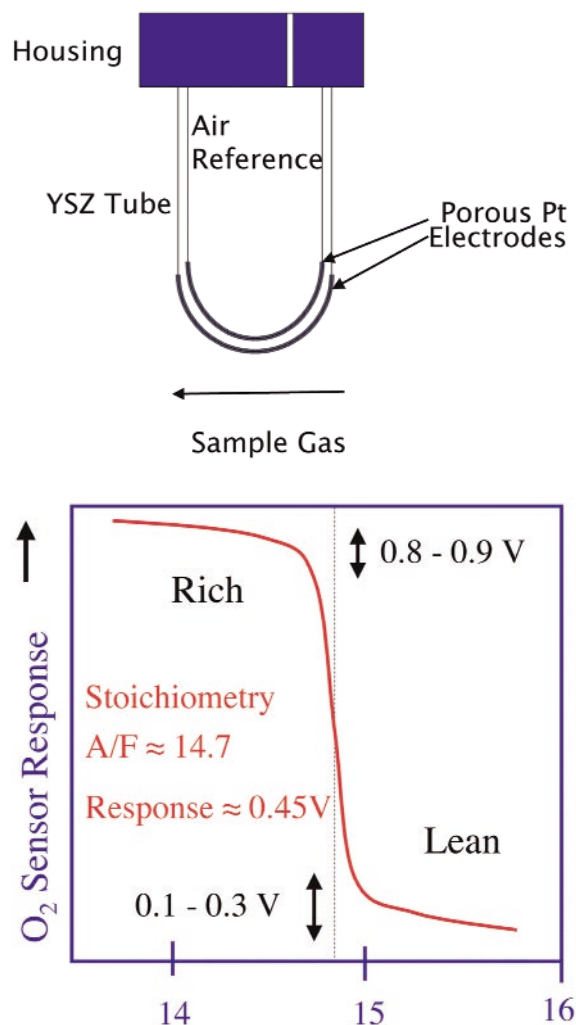


Fig. 1. A schematic of a thimble-type oxygen sensor and the response obtained at various A/F ratios in an automobile.

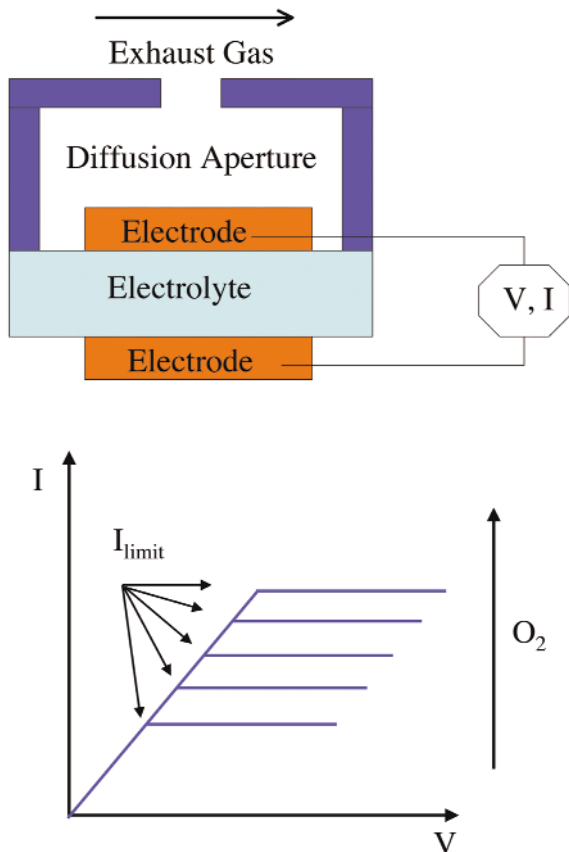


Fig. 2. A schematic of an amperometric oxygen sensor and the typical response obtained at varying oxygen contents.

tial (E) that is related to the thermodynamic oxygen partial pressure of the test gas mixture ($P_{O_2}^{unknown}$) via the Nernst equation (Eq. 1)

$$E = \frac{RT}{4F} t_{ion} \ln \frac{P_{O_2}^{reference}}{P_{O_2}^{unknown}} \quad (1)$$

The sensor consists of a thimble-shaped yttria-stabilized zirconia (YSZ) electrolyte and two platinum electrodes painted on opposite sides where one is exposed to the exhaust gases ($P_{O_2}^{unknown}$) and the other to an air reference ($P_{O_2}^{reference}$).¹⁻³ Theoretically the Pt electrode catalyzes the exhaust gas mixture to thermodynamic equilibrium; however, in practice this is often difficult to achieve.³ A typical response of this sensor is shown in Fig. 1 where the sensor voltage is essentially constant in the lean and rich regions and varies only near the stoichiometric point. The output of this sensor can be used to control the A/F ratio at the stoichiometric point where the three-way catalyst efficiency is a maximum. However, these sensors are not useful in determining the oxy-

gen content in the lean or rich regions where better fuel economy or better performance can be obtained, respectively. There have been several advances in modifying these sensors to make them more sensitive in the lean region, by pumping an oxygen-current (amperometric devices) through the YSZ electrolyte.

A typical amperometric oxygen sensor is configured to produce a mass transport limitation of the oxygen to the electrode/electrolyte interface.⁴ This mass transport limitation is achieved either by a closed cavity with an aperture for gas diffusion or by a diffusion-limiting porous coating covering the electrode. More recently, it has been demonstrated that a dense mixed (oxygen-ion/electron) conducting oxide also may be used as the diffusion barrier.⁵ The oxygen diffusion barrier in these sensors limits the oxygen molecules that come in contact with the electrode/electrolyte interface thereby limiting the oxygen current that can be pumped through the electrolyte. At high pumping potentials, this limiting current ($I_{limiting}$) is proportional to the

oxygen partial pressure of the test gas ($P_{O_2}^{unknown}$) and is given by Eq. 2

$$I_{limiting} = \frac{nFD_{gas}P_{O_2}^{unknown}A}{L} \quad (2)$$

where $n = 4$ is the number of charges transferred for the reaction, F is the Faraday constant, D_{gas} is the diffusion coefficient of the gas, A is the diffusion area, and L the diffusion length. The current output of these devices increases linearly with increasing oxygen concentration under suitable temperature and applied polarization voltages. Figure 2 shows a schematic of an amperometric sensor along with the typical response obtained for such a sensor. An improvement on this amperometric sensor is the universal exhaust gas oxygen (UEGO) sensor, which is a dual oxygen sensor that consists of both a pumping cell and a sensing cell. This dual oxygen sensor also may be used to sense oxygen-containing species by selectively oxidizing various gases on the two anodes by controlling the applied potential to the two cells.⁶

Another type of oxygen sensor that has been developed for the automotive industry is a semiconductor-based oxygen sensor.⁷ These sensors typically are made of TiO_2 , whose conductivity is strongly dependent on the oxygen concentration of the surrounding gases. Catalytic electrodes are incorporated into these sensors to enable them to reach equilibrium with the test gases especially at the lower temperatures. However, these sensors do not have widespread application due to their spotty reliability and accuracy.

A potentiometric oxygen sensor based on the YSZ electrolyte has also been widely used by the utility industry for boiler control. In this case, the sensors incorporate more precious metal (Pt) at the electrodes to achieve equilibrium at the operating temperature. These sensors often incorporate a protective ceramic or metal mesh over the electrode to protect it from the particulate matter present in boiler exhaust gases. Boiler control sensors are more expensive (\approx \$2000) than automotive sensors (\approx \$20) and are more accurate over a wider range of oxygen partial pressures due to higher platinum loadings of the electrodes and better sealing of the reference chamber. These oxygen sensors, although much more robust than the ones in automobiles are still suscepti-

ble to sulfur poisoning. Recent advances have shown that a highly sulfur resistant oxygen sensor can be manufactured by overcoating the Pt electrodes with mixed conducting terbium-doped YSZ.⁸ These novel sensors last over 2 years of continuous operation in a high sulfur environment where a normal Pt-based sensor would fail in less than 12 days.

Sensors for Combustibles and Toxic Gases

Electrochemical sensors have been used since the 1950s to sense various combustible and toxic gases like CO, H₂, NO_x, SO_x, CH₄, and VOCs especially in portable and safety monitors. The most common sensor uses a semiconductor-based technology, where the change in electrical resistivity of a semiconducting material when exposed to certain gases is used to quantify the amount of that gas present. While the most widely used semiconducting material is tin oxide (SnO₂), other materials such as zinc oxide mixed with precious metals, titanium oxide, and tungsten oxide have also been used to detect specific gases.⁹ When a SnO₂ semiconductor is exposed to an oxygen-containing atmosphere, O²⁻ is adsorbed on the surface as an ionized species (O²⁻) with a concomitant loss of electrons from the conduction band of the SnO₂. When this material is then exposed to a reducing gas such as CO, the surface oxygen (O²⁻) is released by a combustion reaction at the surface, which in turn injects electrons into the conduction band thus lowering the surface resistance of this n-type semiconductor. This change in surface resistance can be used to measure the concentration of the combustible gas. If a p-type semiconductor is used, there is an increase in the surface resistance with increasing concentration of the combustible gas.

Semiconductor-type sensors do not possess much selectivity because any gas that changes the surface oxygen content can result in a change in the surface resistance. However, the amount of a particular gas species that is adsorbed on the surface is a strong function of the temperature and composition of the semiconductor. Hence, the sensitivity of these sensors toward a particular gas can be tailored by changing the operating temperature (160°C for H₂, 300°C for CO) or by using different combinations of n- and p-type semiconducting materials (TiO₂

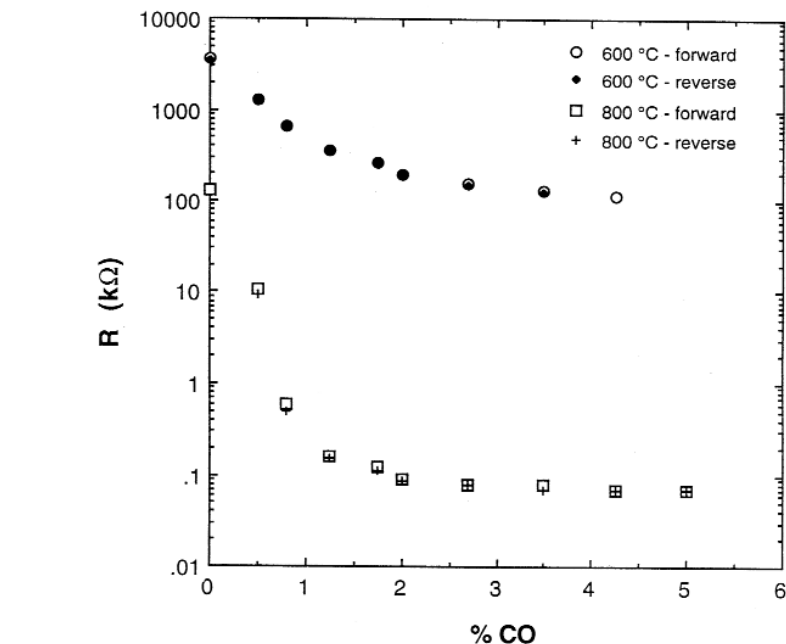


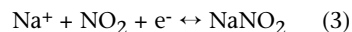
Fig. 3. Response of a TiO₂-based thick-film CO sensor. (Courtesy of Sheikh Akbar, CISM, Ohio State University, Columbus, OH.)

and SnO₂).¹⁰ For example, Fig. 3 illustrates the response of a TiO₂ based semiconductor sensor to changing concentrations of CO in the atmosphere. Moreover, an array of these sensors can be manufactured and the various gases can be identified via pattern recognition software. However, the stability of the sensor response, especially in the presence of changing concentrations of humidity and oxygen content, has limited the usefulness of these sensors for combustion control.

Another type of sensor that is widely used in portable monitors and safety sensors is the low-temperature electrochemical amperometric sensor.¹¹ These sensors use either acid or water based electrolytes and selective electrodes to sense the amount of combustible gases present. For example, to sense CO, a Pt electrode is used in combination with a proton-conducting electrolyte (Nafion). When the CO diffuses to the Pt electrode, it is electrochemically oxidized to CO₂ via the application of an appropriate potential. The current produced by the device can then be correlated directly to the amount of CO present in the ambient gas. The selectivity of these devices is achieved by selecting the potential appropriate to the target gas that is to be oxidized at the anode. Although, these low-temperature sensors have some application in environmental monitoring in the automotive and energy industries, they cannot be used for combustion control where the

temperature of the gases is hotter than the maximum operating temperature of these electrolytes.

Finally, high-temperature potentiometric sensors have also been developed to sense combustible gases. These devices either use an auxiliary phase to fix the potential or operate on non-equilibrium thermodynamics, where the potential is fixed by the kinetic rates of multiple reactions occurring at the electrode. An example of the former type of sensor is a sodium superionic conductor (NASICON) based sensor that has been developed to detect NO_x.^{12,13} The sensor configuration is O₂, Au/(Na⁺)Nasicon/NaNO₂/Au, NO₂, O₂ where the cell reaction is given by Eq. 3



and the sodium ion activity is fixed by the reaction of sodium ions with nitrogen dioxide and oxygen to form sodium nitrite. A limitation of these devices is that the use of auxiliary thermodynamic equilibria as the sensing mechanism leads to a relatively slow response time that is incompatible with combustion control. Moreover, the availability of suitable auxiliary phases has limited the use of these sensors to the detection of few compounds including NO_x, SO_x, and CO/CO₂.

The other type of potentiometric sensor based on reaction kinetics is called the mixed potential, differential catalysis, or non-Nernstian sensor.

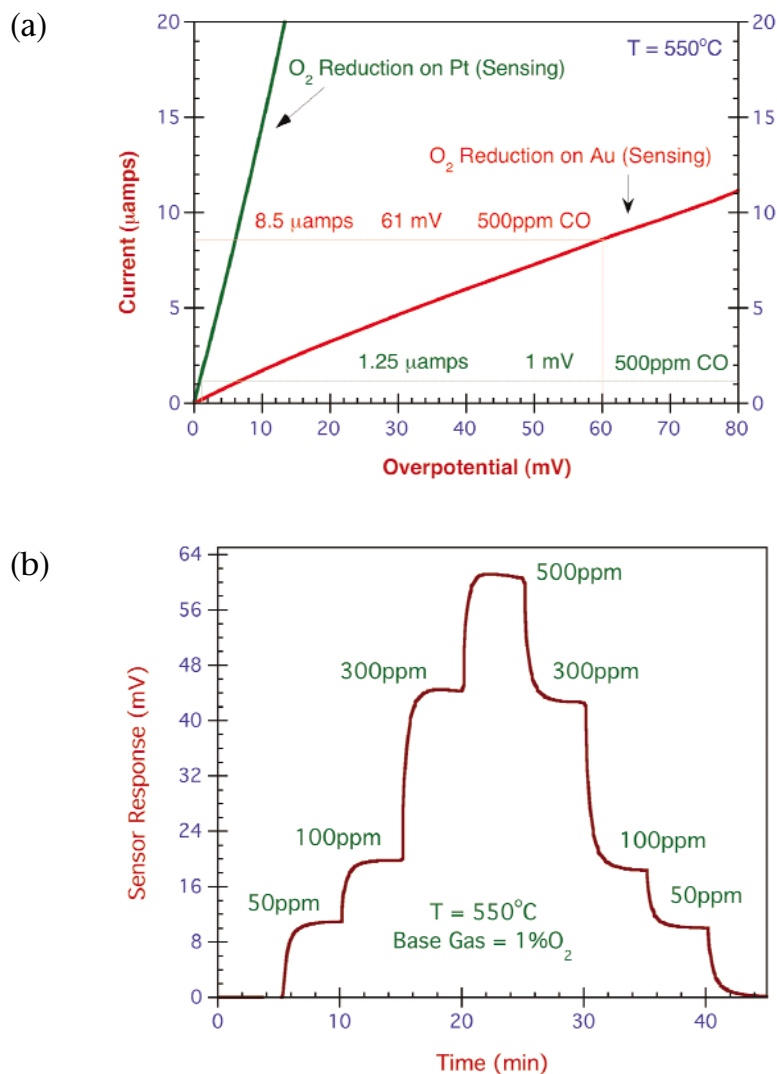
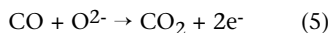
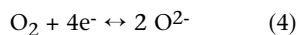


FIG. 4. (a) Polarization curves and (b) CO response of a Pt/Ce_{0.8}Gd_{0.2}O_{1.9}/Au mixed-potential sensor.

These sensors utilize selective electrocatalysis to produce mixed potentials at the electrodes and have been developed to sense various reducing gases including CO, NO_x, and HCs.^{14,15} An example of a sensor of this type is a carbon monoxide sensor that uses two dissimilar electrode materials deposited on a YSZ oxide ion conducting electrolyte.¹⁶ Upon exposure to oxygen and carbon monoxide Reactions 4 and 5 occur at the gas/electrode/electrolyte triple-phase boundaries



The mixed potential is established when the electron-transfer rates of the oxygen reduction Reaction 4 and the carbon monoxide oxidation Reaction 5

are equal. Because these reactions occur at different kinetic rates on dissimilar electrodes, a potential difference is established between two different electrodes that are exposed to the same atmosphere. The successful design of sensors of this type then requires the selection of electrode materials with large differences in electrocatalytic rates for the gases sensed.

Devices that operate on mixed potential mechanisms typically produce output voltages that are much greater than those predicted by thermodynamic equilibrium.¹⁶ The voltage generated is dependent on the reaction kinetics, which can be expressed in terms of the redox current densities, experimentally measurable quantities in many cases. The measured polarization curves for a Pt/Ce_{0.8}Gd_{0.2}O_{1.9}/Au carbon monoxide mixed potential sen-

sor equipped with reference electrodes is displayed in Fig. 4a where the difference in the oxygen reduction rates between the platinum and gold electrodes is the primary source of the mixed potential.¹⁷ Figure 4b displays the mixed potential response of the sensor for varying concentrations of CO.

Mixed-potential sensors have not been used in practical applications due to their lack of stability and reproducibility. Recent advances have solved these problems and opened up the possibility of using these sensors in safety and portable applications.¹⁸ Moreover, several oxide and metal electrodes have been developed that show sensitivity toward specific target gases including HCs and NO_x. However, the dependence of the sensor response on temperature, gas flow rate, and oxygen partial pressure is an impediment in the use of these sensors for combustion-control applications.

HC, NO_x Sensors for Combustion Control

In the automotive industry there is a need to monitor the state of health of the catalyst to meet current on board diagnostics (OBD-II) requirements, which have been in place since 1995-1996. This need is currently met by the use of dual O₂ sensors, one before and one after the catalyst.¹⁹ These sensors measure the O₂ storage capacity of the catalyst, which in turn is an indication of its working efficiency. When the catalyst is working efficiently, it stores oxygen while it reduces the NO_x during the lean cycle and releases that oxygen while oxidizing the HCs during the rich cycle. Therefore, as the engine is cycled through stoichiometry, the oxygen sensor in front of the catalyst shows a cyclic response around the λ-point while the response of the sensor after the catalyst is fairly constant. As the catalyst ages, the post catalyst oxygen sensor starts to show a cycling behavior which becomes identical to the response of the sensor in front of the catalyst when the HC conversion efficiency of the catalyst drops below 60%. This system is only an indirect way of measuring the HC conversion efficiency of the catalyst and does not work when the engine is operated away from stoichiometry. As stricter control of the HC and NO_x emissions from automobiles will be required in the future, there is a pressing need to develop NO_x and HC sensors that work

in the exhaust environment. Moreover, the use of a selective catalyst reduction (SCR) system for NO_x mitigation in diesel engines has made the need for a NO_x sensor for combustion environments more urgent.

Currently, the most advanced NO_x sensor is an amperometric device that has been developed for automotive use.²⁰ This sensor is a modification of the UEGO sensor described in the previous section, where one electrode is modified to be catalytically active toward NO_x reduction. The sensor consists of two zirconia oxygen-pumping cells in conjunction with two aperture-type diffusion barriers. The NO_x and oxygen diffuse through the first barrier onto the first pumping electrode (Au based) that preferentially pumps the O_2 to a predetermined low level ($P_{\text{O}_2} \approx 10^{-4}$ to 10^{-8}) while leaving the NO_x intact to reach the second pumping cell through another diffusion aperture. This second cell preferentially reduces the NO_x over a catalytic electrode containing Rh and the current produced is related to the NO_x concentration of the test gas. Although these sensors measure the

NO_x concentration accurately, they have not been widely deployed due to their high cost and complex design.

Other sensors that have been used for measuring NO_x in portable monitors including semiconductor and mixed-potential types are currently being evaluated for NO_x sensing in automobiles. Single semiconductor (WO_3 -based) sensors do not possess the necessary selectivity, and arrays of these sensors must be used. Moreover, the oxygen partial pressure at the surface of these sensors must be kept constant, which may be achieved by enclosing these sensors within a cavity whose oxygen content is controlled by a zirconia-based pumping cell. However, the stability of these sensors over time and their slow response time are major impediments that must be overcome before they are commercialized.

For, mixed potential sensors, the sign of the response is opposite for an oxidizing gas like NO_2 when compared to a reducing gas like NO. Hence, these sensors must be operated in conjunction with a NO_x reduction/oxidation catalyst or a zirconia-based pumping cell. For

example, the pumping cell or catalyst can be used either to reduce all the NO_x to NO or oxidize all the NO_x to NO_2 . The most advanced of these sensors that has been tested in automobile exhaust environments, is made of a diffusion aperture, a pumping cell to oxidize the NO and HCs, and a mixed-potential sensing cell.²¹ Although this cell works in an exhaust environment and has a much simpler design than the state-of-the-art NO_x amperometric sensors, the stability and reproducibility of these sensors must be improved before they become commercially viable.

Two promising technologies for HC sensing are mixed-potential and microcalorimetric gas sensors. Mixed-potential sensors that respond preferentially to HCs have been developed using oxide electrodes including doped In_2O_3 and lanthanum chromates.²² While recent advances have vastly improved the stability and reproducibility of these sensors, their response is still dependent on the temperature and oxygen content of the test gases. Hence, these sensors must be externally heated and the oxygen content to the sensors must be mea-

sured/controlled—thus leading to increased complexity and cost.

Microcalorimetric sensors have been used to detect HCs by sensing the temperature increase of a low thermal conductivity substrate caused by the oxidation of HCs on a catalyst layer deposited on the substrate. Recently, the sensitivity of these sensors has been improved using silicon micromachining fabrication, which opens up the possibility of their use in an automotive environment.²³ However, the stability of these sensors in these harsh environments must be tested before they can reach their commercial potential.

All the above-described technologies also have application in combustion control for power generation. Currently, various expensive analytical techniques like chemiluminescence, paramagnetic, and infrared are used to monitor the various emissions from utility boilers. Although these sensors help the industry meet government regulations on emissions, few of these provide real-time feedback of the combustion process. If simple, robust, solid-state NO_x, HC, and CO sensors working in harsh combustion environments can be developed, they can greatly improve the efficiency of the combustion process in addition to monitoring the pollutants.

Conclusions

The electrochemical oxygen sensor based on the measurement of the Nernst potential has found widespread application in combustion control of both automobiles and utility boilers. Although it has been more than 25 years since the commercial use of these oxygen sensors began, the deployment of other electrochemical sensors in combustion control has been lacking. The use of sensors in both these industries has been driven more by emissions regulations than by improvements in combustion efficiency. Recent developments have shown that amperometric, semiconducting, calorimetric, and mixed-potential type sensors have the potential to measure the NO_x, HC, and CO content for direct combustion control. These sensors, if successfully commercialized, can lead to real-time optimization of the combustion process that could help not only in reducing emissions but also in improving energy efficiency in both these industries. ■

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