Compact, Bifunctional NO\textsubscript{x}/Oxygen Sensors for High-Temperature Applications (ANL-IN-01-019, ANL-IN-01-019b, ANL-IN-07-094, and ANL-IN-04-105)

Scientists from Argonne and Ohio State University have collaborated to create a low-cost bifunctional high-temperature NO\textsubscript{x}/oxygen sensor that provides real-time sensing inside a combustion chamber without the requirement of a reference air supply.

Background and Need

Industry has sought robust and less expensive sensors that can more accurately monitor and enable control of combustion processes. In certain applications—such as internal combustion engines, coal-fired power plants, petrochemical plants, blast furnaces, glass-processing equipment and industrial burners—greater control can be achieved when sensors are positioned closer to the combustion environment.

Traditionally, sensors in such environments have required an external supply of conditioned air to provide a reference source for determining the constituents of the combustion process. However, this requirement is costly and imposes a maintenance challenge. Ideally, a sensor would be sealed and self-contained, and require no external reference air.
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The Invention

Working together, scientists at Argonne National Laboratory and Ohio State University have developed a compact bifunctional nitrogen-oxides/oxygen (NO\textsubscript{x}/O\textsubscript{2}) sensor. Created by coupling a palladium/palladium oxide internal oxygen reference with two electrochemical techniques, the sensor measures total NO\textsubscript{x} to detect NO\textsubscript{x} and oxygen simultaneously at high temperatures, such as in a combustion furnace. It also avoids the system costs associated with sensors that require a supply of reference air. A high-pressure, high-temperature bonding method creates an effective physical seal of Pd/PdO powder contained in an yttria-stabilized zirconia chamber. Oxygen concentration is obtained from the voltage generated because of the difference in concentration in the internal reference and the combustion environment. A platinum/yttrium filter is used to equilibrate the gas to obtain total NO\textsubscript{x} concentrations. The dissimilarity of catalytic activity between the sensing and reference electrodes generates strong potentiometric signals. This sensor can also measure NO\textsubscript{x} in amperometric mode.

Because the sensor is enabled by an internal reference air chamber, it does not need an external air supply to operate; moreover, it is less expensive than conventional technology. Combination sensors like this one are essential in combustion optimization processes and to successfully monitor nitrogen oxide (NO\textsubscript{x}).

The sensor’s ability to withstand temperatures up to 1600°C permits its placement close to the source of combustion, enabling faster, more accurate monitoring and feedback. This capability also provides the opportunity to accurately map the entire combustion zone.

Eliminating the need for external reference air and joining ceramic components without intermediate bonding materials permits the production of a very compact (millimeter-sized) oxygen sensor, having excellent oxygen conductivity through the housing, at an extremely low production cost (the estimated direct cost of fabrication is less than $200 per unit), with superb stability, very low drift and high sensitivity to changes in oxygen levels.

The information provided by the sensor is important to manufacturers because it helps them optimize their combustion systems and process chemistries. It also enables them to operate economically and use energy efficiently (optimizing the air-to-fuel ratio saves on energy). While various sensors are available, industry has never before had a truly low-cost means of accurately determining NO\textsubscript{x}/oxygen content in the combustion process to achieve the highest-possible energy savings—until now.

Argonne’s plastic deformation bonding method produces a strong, pore-free joint without degrading the materials’ mechanical or electrical properties.

The joining technique relies on the plasticity of the components being joined. A small compressive stress is applied to the two bodies at elevated temperatures (at about half the melting point level). As the two bodies are compressed, grain rotation results from the principal deformation mechanism of grain sliding. As the grains rotate, they inter-penetrate, resulting in a perfect bond with a strength level equal to that of a monolith.

This invention won a 2005 R&D 100 award.

Benefits

This invention offers several benefits over conventional NO\textsubscript{x}/oxygen sensors:

- **Reference air supply.** Not required.
- **Accurate.** Placed directly inside the actual combustion chamber (as opposed to outside the exhaust flue), the sensors offer unsurpassed oxygen-sensing accuracy and extremely low drift.
- **Smaller size.** The sensors are smaller than conventional oxygen sensors and facilitate miniaturization.
- **Economical.** Fabrication costs are substantially lower than that of conventional sensors. Because of their size and cost, multiple sensors can be used in a smaller space.
- **Simpler to operate.** No external supply of reference air is required.
- **Operates at high temperatures.** The sensor body can withstand temperatures of up to 1600°C.
- **Energy-saving.** The sensors optimize the air-fuel ratio and fuel oil viscosity, helping facilities achieve energy savings from 2 to 10 percent.
- **Technology-advancing.** The sensors enable the optimization of next-generation internal combustion engines and coal-fired power plants.
Applications and Industries

- Transportation
- Oil and gas
- Power and steam generation
- Cement
- Pulp and paper
- Industrial process industries
- Blast and glass furnaces
- Internal combustion engines
- Environmental monitoring of exhaust gases

Developmental Stage
Prototypes of the sensors have been built and tested.

Availability/Commercial Readiness
This technology is available for licensing.

Argonne Invention Numbers
ANL-IN-01-019, ANL-IN-01-019b, ANL-IN-07-094, and ANL-IN-04-105

Intellectual Property
United States Patent 6,974,070; 7,413,109; 8,012,323; 8,057,652

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