Solid State Oxygen Sensor for Critical Applications

New solid state oxygen sensor design outperforms traditional zirconium oxide-based sensors, ideal for many specialty gas applications.

by Curt Fauth, President, Delta F

Zirconium oxide oxygen sensors have been around for more than 40 years, and they continue to be incorporated in oxygen analyzers applied successfully to a broad range of applications. More recently, solid state sensors have been developed that have expanded the capabilities of analyzers, permitting them to be applied to many new applications, including specialty gases and critical OEM operations. This article reviews the upgraded solid state sensor technology, as well as its associated benefits, and describes two applications in which the new sensor has demonstrated its versatility and its enhancement of oxygen analyzers.

Solid State Sensor Technologies Compared

Conventional zirconium oxide-based oxygen analyzers typically use air as a reference gas. When a sample gas is fed through them, they produce an output that represents the oxygen partial pressure differential created by the reference gas and the sample gas. This type measurement obeys what is referred to as the Nernst equation, which means that these analyzers have a non-linear (logarithmic) output that needs to be linearized. Also, conventional oxygen analyzers have a variable sensitivity throughout their operating range. In these older analyzers, the sample gas flows through the sensor at some nominal rate (50-100 ml/min is typical), operating temperature is high (~700 C), and the instruments are bulky.

Analyzers with a coulometric ceramic sensor, in contrast, do not require a reference gas, and are energized by an externally supplied current. The result is an analyzer with a linear output and a sensitivity that is constant throughout its operating range.

The solid state coulometric sensor (SSCS) operates much as the wet cell coulometric sensor popularized by Delta F more than 30 years ago. This sensor can operate with or without sample flow, which permits it to be used for in-situ monitoring. This feature is further enhanced by the sensor's small size (it fits into a one-inch cube) and lower operating temperature (in the range of 400 C).

Coulometric Sensor Principle of Operation

The solid state coulometric oxygen analyzer measures oxygen concentration by "counting" the number of electrons flowing through its circuit. The circuit is connected between the sensor's cathode and its anode electrodes. A polarizing dc voltage is used to facilitate the flow of electrons. Oxygen from the sample gas is sensed at the cathode electrode by diffusing through a very small hole in a barrier covering the cathode. (See Figure 1.) Oxygen molecules that come in contact with the cathode are reduced according to the following electrochemical reaction:

$O_2 + 4e^- \rightarrow 2O^{2-}$.

The oxygen ions, O_{2-}, migrate though a solid ceramic electrolyte. Since the solid state electrolyte is a poor conductor at room temperature, it must be heated to 400 C, however this requires only two watts of power. The oxygen ions are converted back to molecular oxygen at the anode electrode. The electrochemical oxidation reaction that takes place at the anode is:

$2O^{2-} \rightarrow O_2 + 4e^-$

The flow of electrons (4e-) between the cathode and anode is proportional to the concentration of oxygen in the sample gas. This current is measured by the analyzer's electronics, and the oxygen concentration is displayed.

Coulometric Sensor Technology Benefits

The solid state coulometric sensor-based analyzer offers several features:

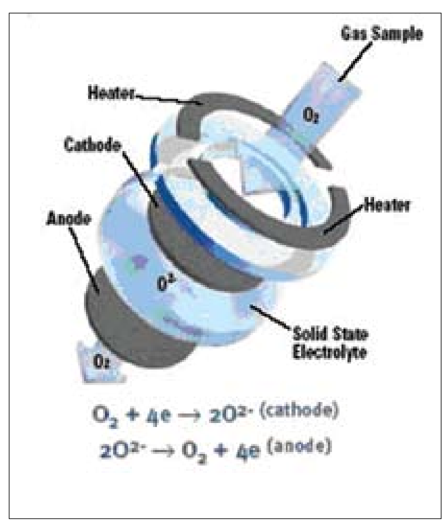

Figure 1. Solid-state Coulometric Sensor

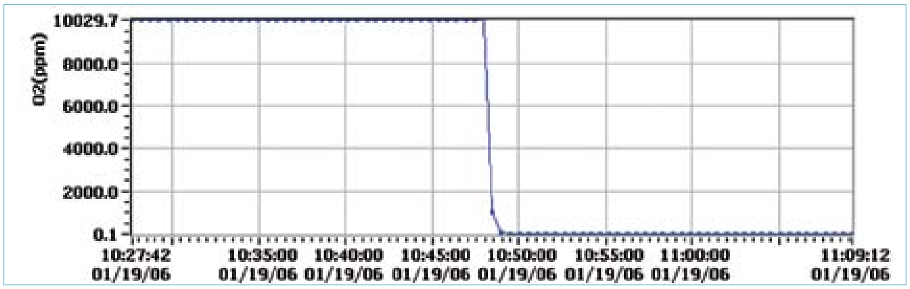

Figure 2. Speed of Response

- *Calibration and Measurement Stability*—Sensors are factory calibrated, which allows the analyzer to be used immediately in the field once it is connected. The non-depleting sensors permit the analyzer to maintain its stability and accuracy for extended periods.
- *Compact Sensor Size*

  The sensor is very compact; it can be fitted into a one-inch cube. Its small size permits it to be packaged for traditional "flow-through" sensing, as well as for in-situ measurement. No pumps or extractive sample systems are required.
- *Broad Ranges of Operation*

  The sensor in available in a wide variety of ranges—0-3000 ppm, 0-10,000 ppm, 0-25 percent, and 0-100 percent.
- *Rapid Speed of Response*

  The ceramic-based oxygen sensor responds rapidly to oxygen partial pressure differentials, yet it is not damaged by oxygen shock, i.e. exposure to ambient air. The 0-3,000 ppm-range sensor can be exposed to air and, in less than one minute, will measure less than 10ppm on pure nitrogen. (See Figure 2.)
- *Linear Response over Range*

  The coulometric solid-state sensor is completely linear throughout its operating range (see Figure 3).
- *No Dependence on Air as Reference Gas*

  The SSCS does not require a reference gas to support measurements. Thus, changes in barometric pressure have no effect on sensor performance.

As with any oxygen sensing technology, this sensor is subject to some limitations. The sensor cannot be used with sample gases that contain hydrocarbons or other combustibles; i.e., H_2, CO, NO_2, S, or Pb. If the analyzer samples contain any of these gases, the analyzer may produce false low readings, or the sensor may be damaged. However, if the hydrocarbon is at a trace level and the oxygen is at a percent level, the reading will not be affected significantly.

Application Examples

Two applications are presented that highlight specific attributes of the solid state coulometric sensor-based oxygen analyzer.

Application No.1—Nuclear Ship Repair

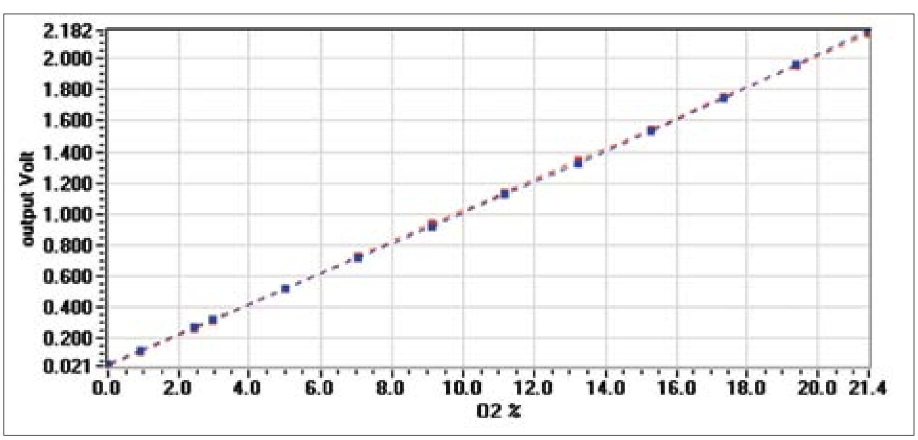

Figure 3. Linearity: Sensor Output vs. Generated Oxygen

Personnel who repair nuclear-powered naval vessels usually follow welding practices established by the *Atomic Energy Commission* or *Nuclear Regulatory Agency* to ensure that quality welds are produced on steel components. Welding is conducted in an argon atmosphere, with the allowable amount of oxygen permitted dependant on the type of steel involved. For high grade steel pipes, the maximum oxygen allowed is typically 0.2 percent or 2,000 ppm, and for lesser grade piping, the specification allows 0.5 percent or 5,000 ppm oxygen. A larger nuclear tank or vessel may be welded with a shielding gas that contains no more than one percent oxygen.

During the welding process, the weld section is covered with a canvas wrap and flooded with argon. An oxygen analyzer is attached to a small vent in the wrap to contain the shielding gas. The piping is then orbitally butt-welded in the inert atmosphere and later X-rayed to ensure the integrity of the weld. If the weld fails to pass inspection, the faulty weld must be cut out and the weld redone—an expensive, time-consuming operation.

Figure 4. Delta F SSCS OEM Analyzer

To perform this operation successfully and economically, several analyzer attributes are required: stable, accurate oxygen readings throughout the welding process; low maintenance requirements (especially recalibration); ability to carry out in-situ measurements; and compact, rugged packaging. A custom analyzer, developed by Delta F for OEM applications, possesses these requisite features, as shown in Figure 4. The solid state sensor has the accuracy, stability, and compact size to easily meet the first set of requirements. The compact size of an analyzer with this sensor permits it to be placed inside the canvas wrap, making it possible to measure the oxygen content directly.

Application No.2—Equipment Protection

The fabrication of semiconductors requires the use of ultra-high purity gases. A common practice in the industry is to use purifiers to clean up gases produced by the cryogenic distillation of air. Some types of purifier media are highly reactive with trace oxygen, however, producing extremely exothermic reactions that generate high temperatures. If the media in the production process is exposed to inordinately high levels of oxygen, the high temperatures resulting from the exothermic reaction can destroy the purification equipment. Even worse, particulate matter and noxious gases can be generated that can affect downstream fabrication processes. At a minimum, this can lead to lost batches of wafers and significant tool downtime—both very expensive experiences.

An oxygen monitor that is placed in the purifier feed stream can detect the onset of an oxygen leak and actuate a relay valve that diverts the purifier input to an off-stream location to avoid downtime, lost product or, worst case, the loss of capital equipment or a fabrication line shutdown.

This application requires an analyzer that can detect the presence of oxygen accurately and quickly. Ideally, the solid state sensor-based analyzer should be mounted upstream of the purifier to ensure a rapid response to oxygen incursions and subsequent temperature rise (See Figure 5.) The analyzer used also must be cost-effective so that it can be built into the system by the OEM.

Figure 5. Remote in-situ sensor.

Summary: The Right Analyzer for the Intended Job

The SSCS has a number of attributes that make it ideal for certain applications. Key are:

- Rapid speed of response
- Quick recovery after air exposure
- Good low end sensitivity
- Consistent accuracy throughout the range of operation
- Linear response throughout the operating range
- Compact size
- Stable calibration over long periods

All of these make it ideally suited to a variety of industrial, specialty gas, and OEM applications.

Acknowledgement

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