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Novel Electrocatalytic Sensors

Fernando Garzon* and Eric Brosha

Abstract

This is the final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The basic principles employed for previously developed oxygen and sulfur dioxide sensors have been applied to other chemical sensor needs. The oxide electrodes used for oxygen sensors also possess novel catalytic properties that have been utilized for the detection of CO through the use of electrocatalysts on solid electrolyte membranes. These metal oxides offer the ability to catalyze reactions selectively for oxidation and/or reduction of analyte gas species. A combination of a catalytic and a non-catalytic electrode deposited on a solid electrolyte was used to sense the reactive species by locally changing the oxygen concentration on the electrode surfaces. Multiple species can be sensed on a single substrate through the use of different electrocatalysts. A related concept is to control the catalytic properties of these materials by controlling the oxygen stoichiometry using an electrochemical pump. The presence of a gas species was sensed by changes in the electronic conductivity of the semiconducting electrode layer.

1. Background and Research Objectives

Carbon monoxide gas (CO) is a deadly, colorless, odorless gas that results from incomplete combustion of typical fuels. It is the most common cause of death among asphyxiant gases in the United States. Better sensor technologies for this gas are needed to protect people in their workplaces and homes. The objective of this project was the development of simple, low-cost electrochemical sensors for the detection of CO in air with tens of parts per million sensitivities, good selectivity, and fast response times. The current commercial sensor technologies cannot detect carbon monoxide below dangerous threshold levels (tens of ppm), nor do they respond quickly at the hundreds of ppm levels.

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2. Importance to LANL's Science and Technology Base and National R&D Needs

This project supports Los Alamos core competencies in earth and environmental systems as well as nuclear and advanced materials. It enhances the visibility of the Laboratory in the area of sensor development and increases our ability to respond to initiatives requiring sophisticated sensors.

3. Scientific Approach and Results to Date

Past research efforts in solid state electrochemical sensors for carbon monoxide detection have used two strategies. In one approach, Williams, *et. al.*, utilized two different noble metal electrodes (one gold and the other platinum) separated by an yttrium-zirconium oxide oxygen-ion conductor (Figure 1). The device operates by the principle that when both electrodes are exposed to the same gas stream containing CO and oxygen, two competing reactions occur on each electrode surface, the reduction of oxygen ($1/2\text{O}_2(\text{g}) + 2\text{e}^- = \text{O}^{2-}$) and the oxidation of CO to carbon dioxide ($\text{CO}(\text{g}) + \text{O}^{2-} = \text{CO}_2(\text{g}) + 2\text{e}^-$). If no current is allowed to flow through the electrolyte, the two reactions on each electrode surface will reach an equilibrium local-exchange current, i.e., the rate of oxygen reduction will equal the rate of CO oxidation. However, the combined reaction rate on the surface of the gold electrode is not the same as the combined rate on the platinum. Since the local exchange-current density depends on surface coverage of several species and on reaction rate constants, these will, in general, be different for different electrode materials. The result is a measured electric potential across the yttrium-zirconium oxide electrolyte due to a difference in oxygen activity (oxygen chemical potential or oxygen partial pressure) across the electrolyte.

The CO sensor reported by Tan, *et. al.*, functions on the same principles discussed in the paragraph above; however, they did not utilize two different metal electrodes to provide differing oxidation and reduction (redox) rates across an oxygen ion conductor. Instead, they used two platinum electrodes. The different redox rates were obtained by coating one of the platinum electrodes with a mixture of CuO and ZnO (Figure 2). This two-phase mixture of the oxides of copper and zinc is a known CO oxidation catalyst. As above, the differing rates of CO oxidation lead to a difference in oxygen chemical potential across the solid electrolyte, which leads to a measurable response in the form of an electric potential across the sensor.

The operating principle behind our sensor is the same as that of Williams and Tan. Our sensor design differs in that we utilized a fully dense thin film of a mixed electronic and ionic conducting and catalytic metal oxide, such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, deposited by an RF magnetron

sputtering vapor deposition process onto a thin yttrium-zirconium oxide solid electrolyte (Figure 3). A thin film of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, approximately 1000-2000 Å thick, is necessary to ensure a fast response to CO. The sensor response characteristics of thick films (on the order of 1 μm thick) begin to degrade due to the large oxygen storage capacity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$. The use of a thin electrolyte also improves response time. We used 500 μm-thick CeraFlex brand electrolyte cut to 1 cm² pieces. The perovskite $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ is used because it exhibits intrinsic catalytic activity for the oxidation of CO. This property is probably the result of strong cobalt ion-carbon monoxide ligand interactions. Since $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ is an electronic conductor, no auxiliary metal electrode is required. The counter electrode is a sputtered film of gold, which is a poor CO oxidation catalyst, approximately 2500 Å thick. The response time of this sensor to carbon monoxide is shown in Figure 4. Note the small response to relatively high concentrations of hydrogen, a very reactive interference gas.

This configuration offers several performance advantages over those designs presented by Tan and Williams: (1) increased sensitivity; (2) higher operating temperatures, and thus a wide operating window; and (3) faster response time. Figure 5 is a plot that compares CO response data from Tan, *et. al.*, (which is superior to the Williams device) to our data. Both sets were acquired at 500 °C and in an air background. Although our data were taken at a lower CO concentration range (less than 500 ppm), the data indicate a much larger response output voltage and a greater slope. This indicates that our sensor design offers greater sensitivity to small quantities of CO. The linear response in this CO concentration range is also highly desirable from an applications viewpoint.

The use of a metal oxide as a sensing electrode extends the operating temperature range. Figure 6 is a plot of our sensor compared to Tan, *et. al.*, as a function of increasing temperature. Although the sensor output decreases with increasing temperature for both sensor designs, our sensor still exhibits appreciable sensitivity even at 700 °C. Tan, *et. al.*, examined the effect of increased temperature on their sensor output. They report that the maximum output obtained in air occurred around 350 °C. However, the lowest useful temperature range appears to be 400-450 °C, as the sensor response time greatly increases with decreasing temperature. Their data indicate that by 550 °C, the sensor output decreased by 90% of the output recorded at 400 °C. It is important to emphasize that the output of our sensor at 700 °C exceeds the output reported by Tan, *et. al.* at 500 °C.

Our sensor offers not only a greater operating window, and thus an increased flexibility for use, but a faster response time as well. The response-time data reported by Tan indicates a 4-minute period is required to reach an equilibrium voltage value, as compared to a approximately 10-second response time for our sensor. This improvement in response time is

attributable to the use of a mixed conducting-metal oxide as a sense electrode, use of a thin electrolyte, and operation at a higher temperature.

We also report the effect of current biasing on sensor response. The application of a small current bias to our sensor can preferentially improve or degrade the response depending on current-flow direction with respect to the metal oxide electrode. Figure 7 is a plot of CO response of our sensor taken at 500 °C showing the effects of current biasing. The application of +0.15 μA increases sensor output by almost 20 mV. By biasing the sensor such that oxygen ions flow through the electrolyte toward the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ film, the rate of CO oxidation is enhanced with respect to the rate of oxygen reduction on the gold surface. The result is an increase in sensor output because of an increased oxygen differential across the electrolyte. Reversing the current reverses the process, so that $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ becomes a poor CO oxidation catalyst and the sensor response decreases.

We have developed state-of-the-art, low-cost, solid-state electrochemical sensors with good selectivity, sensitivity, and fast response times to carbon monoxide gas. This technology appears to be very promising for commercialization to CO safety monitor systems.

Figure 1. Mixed potential sensor reported by Williams, *et. al.*

Figure 2. Carbon monoxide sensor reported by Tan, *et. al.*

Figure 3. $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ -based CO sensors developed by the authors.

Figure 4. Sensor response at 650 °C to hydrogen (interference gas) and varying concentrations of CO in air.

Figure 5. A comparison of CO sensor output between the authors' sensors and sensors of Tan, et. al., at 500 °C and in an air background.

Figure 6. Temperature dependence of sensor response versus CO level. Data from the authors are plotted with line fits.

Figure 7. The effect of current biasing on a $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ -based CO sensor.