

GAS SENSORS FOR FOSSIL ENERGY APPLICATIONS

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ABSTRACT

Recent advances in SO_x sensor development at The Oak Ridge National Laboratory have demonstrated that a simple, single material, electrochemical sensor can measure SO₂ concentration between 1 and 100 ppm at temperatures between 600 and 900°C. This new solid state sensor operates much like a mixed potential sensor and has been optimized to have no baseline drift, an issue that has plagued many solid state sensors. In our mixed potential sensor the difference in catalytic response between two different electrode materials provides a "differential electrode equilibria" (mixed potential sensor) to selectively measure SO₂. ORNL has developed a novel electrode design and configuration has led to the elimination of the baseline drift. Recent work has demonstrated that interferences such as CO, NO₂, and NO do not alter the sensor output. Future work will focus on the contribution of steam and oxygen to the sensor signal.

INTRODUCTION

Sulfur dioxide (SO₂) is produced by the combustion of sulfur-containing fuels such as coal. Although most of the SO₂ thus produced can be captured with limestone (or other techniques) good environmental stewardship demands that combustion exhausts be monitored for the release of this gas. It is important that SO₂ release be minimized because this compound will form sulfuric acid (H₂SO₄, the principal component of acid rain) when mixed with the O₂ and H₂O naturally present in the earth's environment as shown in Fig. 1.

Currently most SO₂ monitoring is done using ultraviolet (UV) fluorescence, a technique that offers excellent precision and selectivity but requires complex and expensive instrumentation. It also requires the gas to be cooled to near room temperature, thus introducing potential difficulties with condensation [1]. Hence attention has been focused on electrochemical sensors owing to their ease of fabrication, high sensitivity, rapid response, online monitoring and the feasibility for miniaturization [2,3]. In the last 5 years numerous approaches [4-20] to measure SO₂ concentrations in gas streams have been investigated. Most of these approaches have issues

limiting their development and deployment as functional SO_x sensors and none have resulted in a viable sensor.

In this research our objective is to develop compact and inexpensive SO₂ sensors that can operate at high temperatures (~700–900°C). Development of such a sensor would offer three advantages:

1. The need to cool the exhaust gas would be eliminated.
2. Operation closer to the combustion zone would be enabled.
3. The cost of the sensor would be reduced.

EXPERIMENTAL APPROACH

The most successful examples of compact and inexpensive sensors that operate at high temperature are the "lambda" O₂ and pumping-type NO_x sensors developed for transportation applications. Therefore our development efforts have been centered on similar materials and techniques for the detection of SO₂. In particular, we are developing SO₂ sensors that are based on yttria-stabilized zirconia (Zr_{1-x}Y_xO_{2-2x} where x=0.16), an oxygen-ion conducting solid electrolyte that offers excellent stability at high temperature.

In FY 06 it was found that YSZ-based sensing elements with a reasonably simple geometry offered excellent response to SO₂ but addition of steam to the gas stream (as would be encountered in actual operation) led to unstable and non-reproducible behavior. The baseline drift and the effect of interferents such as hydrocarbons and carbon monoxide also needed to be characterized (and subsequently minimized). Therefore, at the onset of FY 07 our objectives were threefold in nature:

1. Develop alternative materials and/or operating conditions that enable stability in the presence of steam.
2. Characterize/minimize the baseline drift.
3. Characterize/minimize the response to interferents.

RESULTS AND DISCUSSION

Two steps were taken in order to improve the stability of the sensor elements in steam: One of the electrode materials was changed from a Mg-modified lanthanum chromite to a Sr-modified lanthanum manganite, and the operating temperature of the sensing element was increased from 750 to 800 °C. This resulted in the performance shown in Fig. 2. There it can be seen that water vapor does have a small effect on the sensor response to SO₂, but the presence of H₂O no longer affects the baseline as was the case previously.

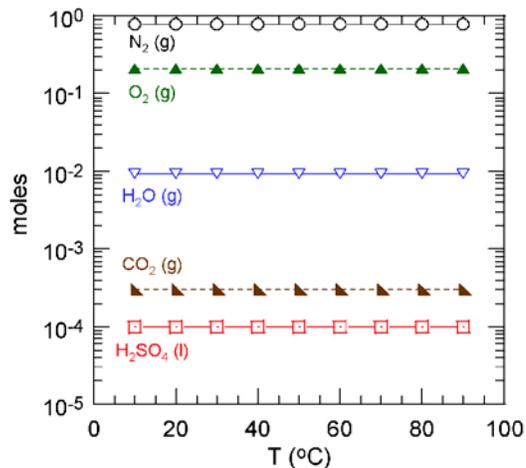


Figure 1: Predicted equilibrium species in a mixture of (in mol) 0.79 N₂, 0.21 O₂, 0.01 H₂O, and 1 x 10⁻⁴ SO₂. The sulfur is all present as sulfuric acid (H₂SO₄).

“Drift” is often a problem with gas sensors and, as mentioned above, the drift behavior of these developmental SO₂ sensing elements was not well characterized at the beginning of FY 2007. Experiments early in the fiscal year showed that zero drift occurred in these sensors, as illustrated in Fig. 3. Two strategies have been employed to combat this drift, with the first being the introduction of a third electrode. As Fig. 4 shows, using this electrode as a “reference” reduces the drift significantly. We believe the reduced drift is a result of less net electromigration at the measuring electrodes (no current is passed through the reference electrode). The second strategy, a much more recent development than the first, is to adopt a sensing modality that does not involve application of an electrical stimulus to the sensing element. This modality has shown excellent response to SO₂ with minimal drift at about 600 °C and will be investigated further in the future if funding continues on this project.

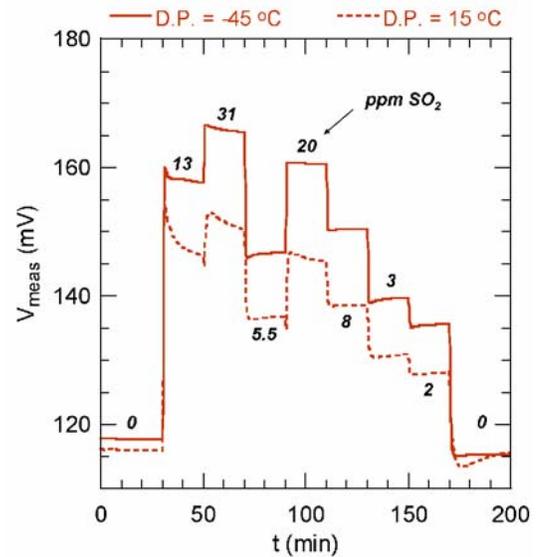


Figure 2: Sensing performance in “dry” (-45 °C dew point) and “wet” (15 °C dew point) gas. Data collected at 800 °C with 7 vol% O₂, balance N₂.

Since these sensing elements are designed to be operated in combustion exhausts, cross-sensitivity to interfering gases such as carbon monoxide and dioxide is a concern. To characterize this behavior, the sensing element of Fig. 4 was subjected to various interferents. The resulting data is shown in Fig. 5, and it can be seen there that the response to interferents is relatively small compared to the response to SO₂. (For example, referring to Fig. 5, 300 ppm of propylene (C₃H₆) induces about a 5% change in V_{meas}.) From Fig. 4, an order of magnitude smaller amount of SO₂ (~10 ppm) induces about a 5% change in V_{meas}. Therefore we consider these sensing elements to display minimal cross-sensitivity.

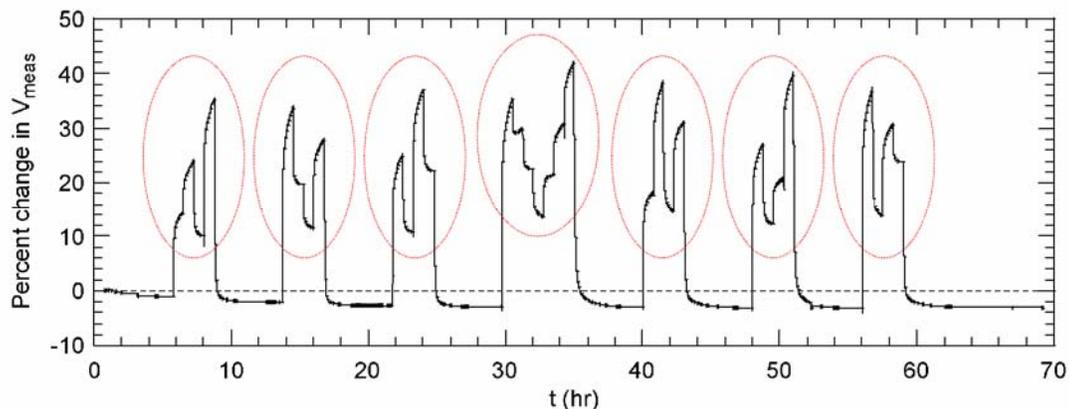


Figure 3: Drift of sensor response with a 2-electrode element configuration. The input SO₂ concentration was varied (in random order) between 2, 5.5, 13, and 31 ppm in the circled regions. T_{oper} = 900 °C with 7 vol% O₂, 1.2 vol% H₂O (~10 °C dew point), balance N₂.

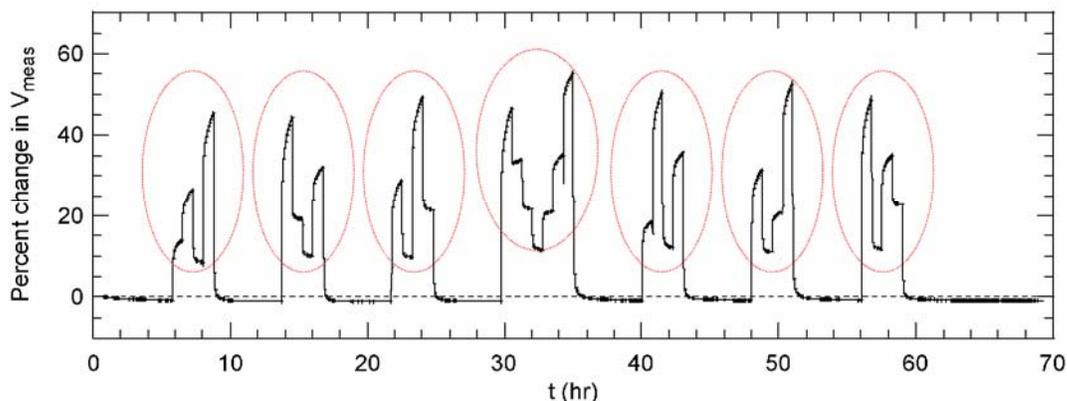


Figure 4: Drift of sensor response with a 3-electrode element configuration. The test regimen was identical to that used for the data in Fig. 3 above.

CONCLUSIONS AND PLANNED FUTURE WORK

We have been successful in developing compact SO_2 sensing elements that are capable of operation at elevated temperature ($\sim 800\text{--}900\text{ }^\circ\text{C}$). The response to SO_2 is strong and readily measurable for SO_2 levels in the 10 ppm range and the effects of potential interferences such as carbon monoxide are comparatively small.

The future work we have planned on this project (contingent on further funding) includes testing at higher steam levels, further studies of long-term stability, and incorporation of the sensing elements into prototype "off the shelf" sensors. We will also explore the different sensing modality mentioned above in the discussion of baseline drift.

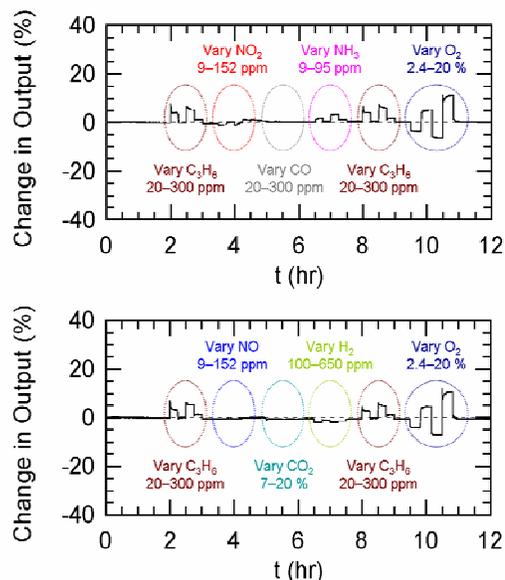


Figure 5: Response to various interfering gases. $T_{\text{oper}} = 900\text{ }^\circ\text{C}$ with 7 vol% O_2 (except where indicated), balance N_2 .

ACKNOWLEDGEMENTS

The authors would like to thank B. Armstrong for assistance in sample preparation. Research sponsored by the Department of Energy's Fossil Energy Program. Oak Ridge National Laboratory (ORNL) is managed by UT-Battelle, LLC for the U. S. Department of Energy under Contract No. DE-AC05-00OR22725.

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