Structural Analysis of Bosch Heated Exhaust Gas Oxygen Sensors After Voltage Treatments

Regina Blackman[1], Arwa Alshowaier[2], Erica P. Murray[2]

[1]Department of Chemistry, Francis Marion University

[2]Institute for Micromanufacturing, Louisiana Tech University

Abstract

Heated Exhaust Gas Oxygen Sensors are used to detect the emissions of the everyday vehicle. Applying a voltage to these sensors simulates the conditions that the sensor is under when in a vehicle. Experiments show that when a voltage is applied for a long enough time, blackening occurs around the electrodes. By performing voltage treatments, it is possible to define the conditions that cause blackening. It is also possible to see the changes in the structure of the Yttria Stabilized Zirconia (YSZ) by cutting the sensor and looking at it under a Scanning Electron Microscope. Looking at the cut sensor under an optical microscope allows for the design of the sensor to be examined and measurements to be taken.

Introduction

Heated Exhaust Gas Oxygen (HEGO) sensors are used to detect the oxygen emissions from engines. These sensors help to optimize air-fuel ratio within the engine. The correct air-fuel ratio helps to prevent engine misfire and wasted fuel. HEGO sensors are composed of platinum electrodes encased in an Yttria Stabilized Zirconia (YSZ) electrolyte. When a large voltage is applied to this YSZ, it becomes blackened. Blackening is caused by a strong chemical reduction, or when oxygen is taken from the lattice structure [3,4]. Using an optical and a Scanning Electron Microscope, this change in the lattice structure or blackening can be readily observed.

Procedure

Bosch Heated Exhaust Gas Oxygen (HEGO) Sensor samples were placed in the sensor housing. Ten samples were examined; heat as well as voltage applied to each one as shown in Table 1. The heat was applied using a regulated DC power supply, where the voltage was applied using a single output programmable DC power supply. After the voltage treatment, the samples were cut using a low speed saw. The samples were then examined using X-Ray Diffraction, a Scanning Electron Microscope, and an optical microscope at various magnifications.

Results

Figure 1 shows the sensor. The red circle is where the sensor heats up (fraction 8). The black circle is where the sensor is placed into the housing (fraction 1). These two fractions were compared in using the Zeta 3D microscope. Using this microscope enabled us to measure the changing hole size, as well as see the sensor better. Figure 2 shows the images of sample 6 using this microscope. The picture to the left is fraction 1, where the picture to the right is fraction 8, where the voltage and heat are applied. Showing these pictures side-by-side enables the changing hole size to easily be seen as well as the orientation of the electrodes to be determined. In fraction 1, there are two platinum heater electrodes, seen on the left side of the hole. When looking at fraction 8, there are four platinum heater electrodes. Sample 6 was the first of two blackened samples (samples 6 &7). The blackening is the discoloration seen in the picture on the right. Figure 3 shows the raw sample. There is no noticeable difference in size of the hole, and there is no discoloration from one fraction to another. Figure 4 shows the Scanning Electron Microscope (SEM) images of Sample 6. This compares the structure of the sample. The image on the left shows fraction 6, which is not blackened. The image on the right shows the blackened fraction 8. Figure 5 shows the X-Ray Diffraction (XRD) data comparing Sample 6 to the Raw Sample. The counts of Yttria Stabilized Zirconia (YSZ) are significantly less in the blackened sample.

Table 1: Voltage, Temperature, and Time of Voltage Treatments for 11 Samples. Highlighted Samples are Blackened

Sample Number	Voltage (V)	Temperature (°C)	Time Period (hrs)
1	2	400 (9 V)	4
2	Raw Sample (No Voltage Treatment)		
3	2	400 (9 V)	2
4	2	400 (9 V)	3
5	2	400 (9 V)	4
6	**3**	**400 (9 V)**	**1**
7	**3**	**700 (18 V)**	**0.333**
8	2	750 (20 V)	4
9	2.8	750 (20 V)	1
10	2.6	750 (20 V)	3.5
11	2.9	750 (20 V)	2

Figure 1: HEGO Sensor. Sensor Side and Heater Side. Blackening occurs in the area circled in red.

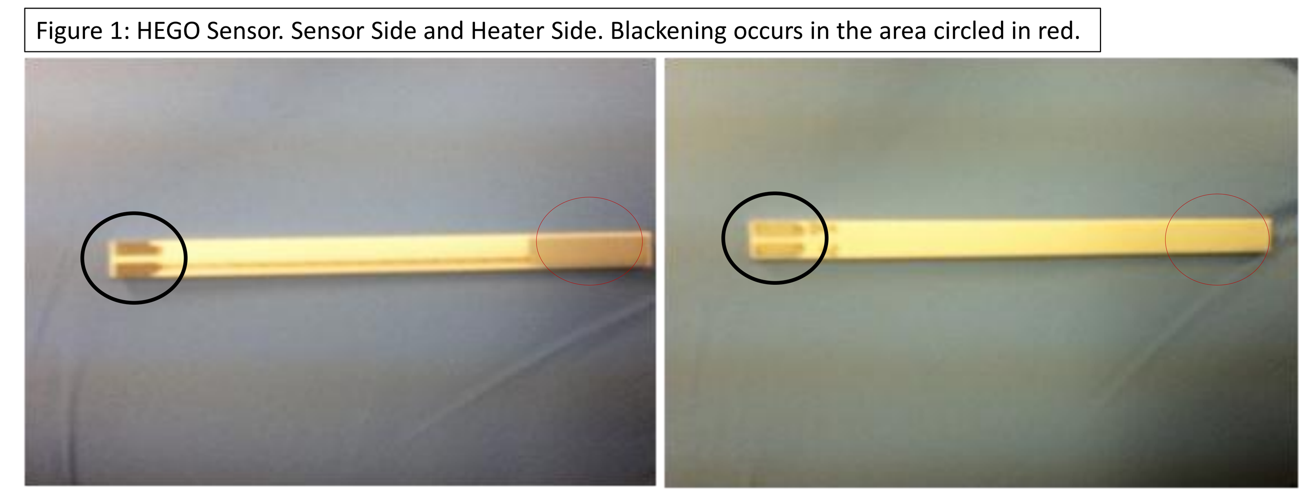


Figure 2: Sample 6, fractions 1 & 8. Note the difference in hole size, as well as color.

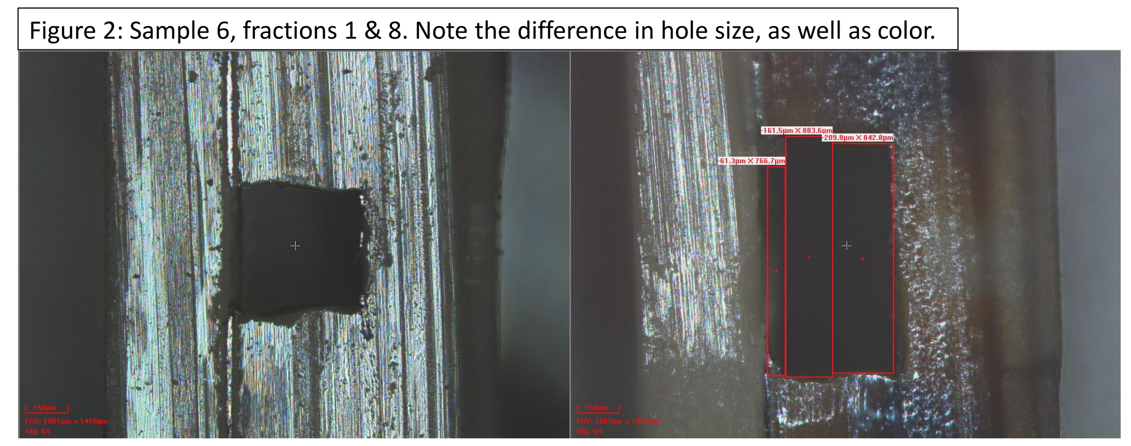


Figure 3: Raw Sample, fractions 1 & 8. The hole has no noticeable difference in size.

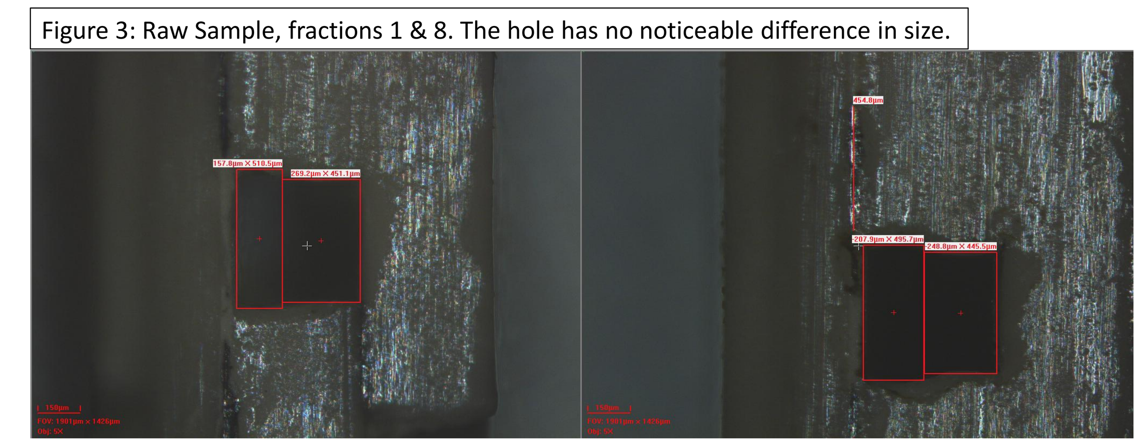


Figure 4: SEM images of Sample 6, fractions 6 & 8. Note the difference in structure.

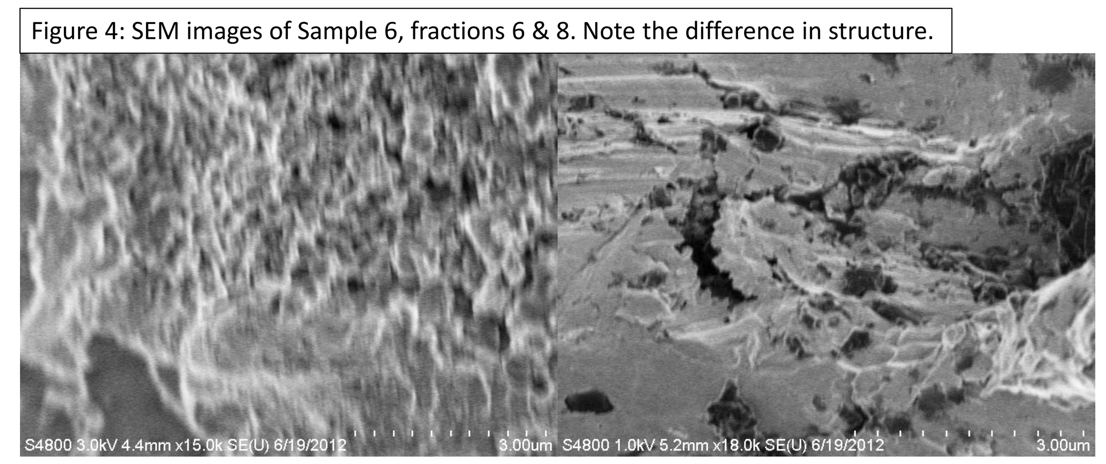
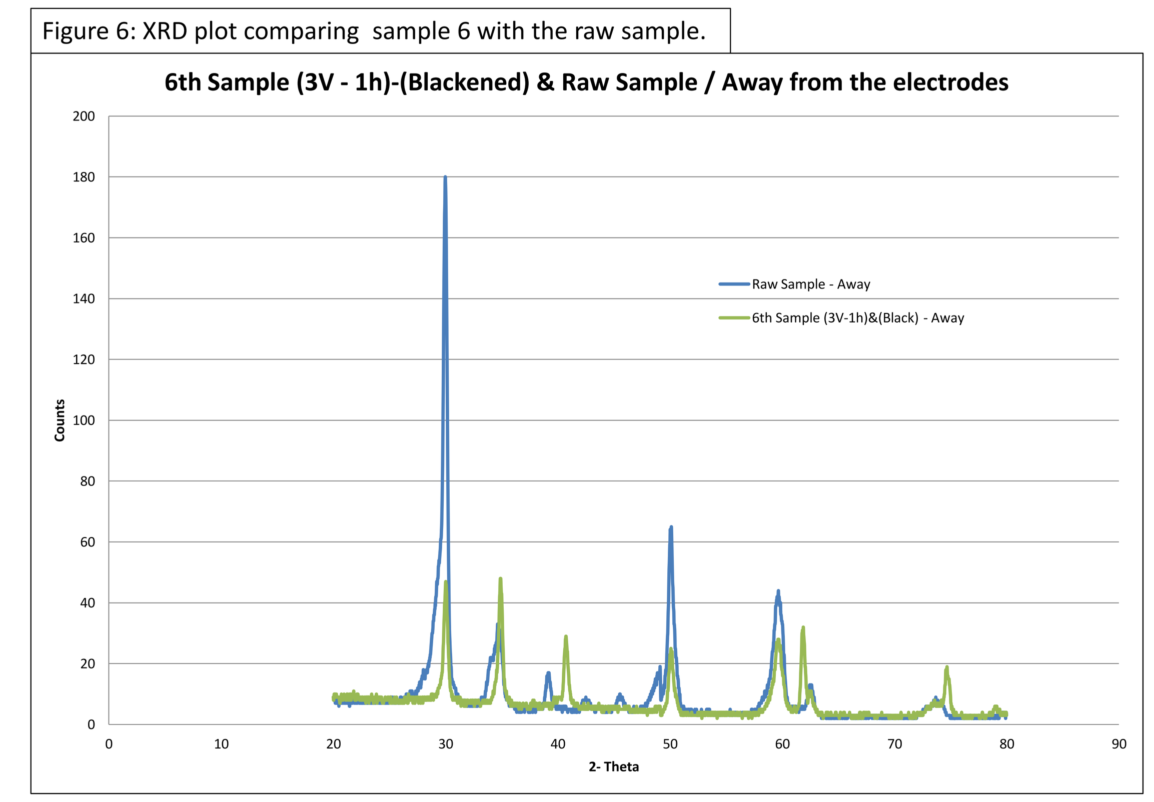


Figure 6: XRD plot comparing sample 6 with the raw sample.



Conclusion

The oxygen that is removed from the lattice structure may affect the functionality of the HEGO sensors. Further research on this will help to define the conditions under which the YSZ becomes blackened. Of the 10 samples that were treated, only two were blackened. From this, it is easy to define the upper threshold of the parameters. When the sensor was treated at 3V, there were signs of blackening, occurring faster and more spread out when the temperature was raised from 400°C to 700°C. Also, the images from the optical microscope help to determine where the blackening is occurring. The blackening is affecting the area around the sensor electrodes. It starts on the inside of the heater electrodes and is blackened through to the opposite side of the sensor electrodes.

Future Work

- Further examination using the Zeta 3D microscope
- Determining the cause of the expanding hole
- Discovering what happens to the YSZ when the hole expands
- Determining the parameters of the HEGO Sensor

References

[1] Butz, B., R. Schneider, D. Gerthsen, M. Schowalter, and A. Rosenauer. "Decomposition of 8.5 Mol.% Y_2O_3-doped Zirconia and Its Contribution to the Degradation of Ionic Conductivity." *Acta Materialia* 57 (2009): 5480-490. *Science Direct*. Web. 30 May 2012.

[2] Hattori, Masatoshi, Yasuo Takeda, Yoshinori Sakaki, Akihoro Nakanishi, Satoshi Ohara, Kazuo Mukai, Jin-Hoo Lee, and Takehisa Fukui. "Effect of Aging on Conductivity of Yttria Stabilized Zirconia." *Journal of Power Sources* 126 (2004): 23-27. *Science Direct*. Web. 30 May 2012.

[3] Nazarpour, S., C. Lopez, F. Ramos, and A. Cirera. "Structural and Electrical Properties of Y-doped Zirconia Induced by Electrical Polarization." *Solid State Ionics* 184.1 (2011): 19-22. *Science Direct*. Web. 30 May 2012.

[4] Nazarpour, S., C. López-Gándara, F. M. Ramos, C. Zamani, A. Cirera, and M. Chaker. "High Temperature Phase Stability and Chemical Analysis of the Highly Doped Yttria-stabilized Zirconia with Alumina." *Ceramics International* 38 (2012): 4813-818. *Science Direct*. Web. 6 June 2012.

Acknowledgements

This material is based upon work supported by the National Science Foundation under the NSF EPSCoR Cooperative Agreement No. EPS-1003897 with additional support from the Louisiana Board of Regents.