

Zirconia-Based Mixed Potential CO/HC Sensors with LaMnO<sub>3</sub> and Tb-doped YSZ Electrodes

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ABSTRACT

We have investigated the performance of dual metal oxide electrode mixed potential sensors in an engine-out, dynamometer environment. Sensors were fabricated by sputtering thin films of LaMnO<sub>3</sub> and Tb-doped YSZ onto YSZ electrolyte. Au gauze held onto the metal oxide thin films with Au ink was used for current collection. The exhaust gas from a 4.8L, V8 engine operated in open loop, steady-state mode around stoichiometry at 1500 RPM and 50 Nm. The sensor showed a stable EMF response (with no hysteresis) to varying concentrations of total exhaust gas HC content. The sensor response was measured at 620 and 670°C and shows temperature behavior characteristic of mixed potential-type sensors. The results of these engine-dynamometer tests are encouraging; however, the limitations associated with Au current collection present the biggest impediment to automotive use.

INTRODUCTION

Today's automobiles use a potentiometric oxygen sensor in the exhaust manifold as part of a feedback control system to control the air-to-fuel ratio. Stoichiometric engine control allows the three-way catalytic converter to oxidize hydrocarbons (HCs) and CO while simultaneously reducing oxides of nitrogen (NO<sub>x</sub>). A second oxygen sensor located downstream of the catalytic converter is used in conjunction with the first oxygen sensor to infer the catalyst HC conversion efficiency as part of an On-Board Diagnostic (OBD) system. In this measurement, the oxygen storage capacity of the catalyst is determined, which is used as an indirect measurement of the HC conversion efficiency. A direct measurement of the concentration of hydrocarbons may result in a better OBD system in future vehicles, which need to comply with even more stringent emissions standards. Furthermore, the current method of OBD HC catalyst efficiency monitoring will not work with lean burn engine technology, because the A/F ratio is no longer controlled around stoichiometry.

Mixed potential sensors based on oxygen ion conducting electrolytes have been investigated extensively for the detection of CO, H<sub>2</sub>, HCs, and NO<sub>x</sub>. The competing

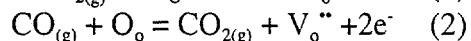
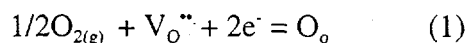
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reactions of oxygen reduction (oxidation) and CO or HC oxidation (reduction) establish the mixed potential at an electrode. Equations 1-2 illustrate this for CO.



In these equations,  $\text{V}_\text{o}^{\bullet\bullet}$  is an oxygen vacancy and  $\text{O}_\text{o}$  is a lattice oxygen in the electrolyte. Depending on the rates of the two reactions, a non-equilibrium potential that is more negative than that predicted by the Nernst equation develops under oxygen rich conditions (1). This mixed potential, being dependent on kinetic factors, is expected to be a strong function of the electrode material (2).

The first reported mixed potential sensor utilized an yttria-stabilized zirconia electrolyte with gold and platinum metal electrodes (3). Since then, many other groups have investigated mixed potential sensors based on oxygen ion-conducting solid electrolytes for the detection of CO, H<sub>2</sub>, HCs, and NO<sub>x</sub> (1-16). We have explored the use of mixed potential sensors based on dual metal oxide electrodes for automotive applications (16). We continue this work with emphasis on selecting refractory metal oxide electrode/electrolyte materials and sensor designs that will withstand the rigors of the automobile exhaust environment.

## EXPERIMENTAL

Cera-Flex™ brand yttria-stabilized zirconia, obtained from Marketech International in 0.5x100x100 mm sheets, was ultrasonically cut into 0.5 in. dia. round. Substrates were cleaned and then mounted onto a Ni faceplate of a heater box using pins that held the substrate in contact against the heated surface. This configuration permitted sputter coating both sides of the substrate without the need for silver epoxy and avoided potential contamination from the epoxy. The Ni heater faceplate temperature was monitored using a thermocouple embedded with in the faceplate. The heater assembly was placed into an ultra-high vacuum sputter system. Depositions were made using 90° off-axis radio frequency (RF) magnetron sputtering technique from a single 2-in. powder target. The LaMnO<sub>3</sub> (LMO) and Y<sub>0.16</sub>Tb<sub>0.30</sub>Zr<sub>0.54</sub>O<sub>2-δ</sub> (TbYSZ) target powders were made using standard solid state reaction techniques. The powders were packed into copper sputter cups and mounted into the sputter gun in the same manner as a hard target. The sputter conditions for both LMO and TbYSZ film depositions were 90° off axis, a 700°C heater faceplate temperature, a chamber pressure of 40 mTorr of a 40% O<sub>2</sub>/ 60% Ar gas mixture and a RF power of 100 watts. The deposition time was 45 minutes for each side. The particular heater faceplate configuration used in this work precluded the use of a sapphire witness sample and subsequent use of a profilometer to determine film thickness. The film thickness was estimated to be approximately 2500Å by repeating the sputter process on shadow-masked, polished sapphire substrates. The film thickness of these calibration runs was measured using a stylus profilometer (DEKTAK).

Once the metal oxide electrodes were completed, a thin coat of Au ink (Electro-Science Laboratories, Inc. 8880-H) was applied first to one side of the device to an area of approximately 4 x 4 mm. Before drying, a small square patch of Au gauze (52 mesh woven, 0.1 mm dia wire) was pressed onto the patch of Au ink. The sensor was heated to 125°C for 10 to 15 min to dry the ink. The temperature was raised at 60°C/min to 900°C

and held there for 1 hr to anneal the Au ink. This process was repeated for the opposite side of the device. Figure 1 shows an illustration of the sensor. Au wires, 0.010" were bonded to a portion of the Au mesh using a parallel gap welder. The sensor and the attached Au leads were placed into a holder that was machined out of macor ceramic (MACOR, Corning Glass). The Au leads were threaded through a 3 mm diameter two-bore alumina tube. The sensor element was immobilized using a macor plug with threads machined into the plug and body. See Figure 2 for an illustration.

Gas mixing in the laboratory was carried out using MKS flow controllers. A 1% O<sub>2</sub>/99% N<sub>2</sub> gas mixture flowing at 200 to 500 sccm was used as a base gas. The test gases were typically 2500 ppm diluted in N<sub>2</sub> with no O<sub>2</sub> present. Therefore, when mixed into the base gas stream to obtain the desired concentration, the PO<sub>2</sub> was slightly reduced. An Amatek O<sub>2</sub> analyzer used to measure PO<sub>2</sub> levels.

## RESULTS AND DISCUSSION

Figure 1 is an illustration of a mixed potential sensor that utilizes RF-sputtered thin films of La-Mn-O and Tb-doped YSZ mixed-conducting oxides and a YSZ electrolyte. A Au gauze current collector held in place using Au ink accomplishes current collection. Figure 2 shows an illustration of the packaging used to hold the sample for the dynamometer experiments.

Figure 3 is the response of a Au/LaMnO<sub>3</sub>/YSZ/Tb-YSZ/Au device tested under laboratory conditions at 650°C. The base gas composition was 1.8%O<sub>2</sub> with N<sub>2</sub> as the balance gas. This level of O<sub>2</sub> would correspond to lean engine conditions. As noted in the figure, the test gases were C<sub>3</sub>H<sub>6</sub> and CO. Mixed potential sensors using Au and LMO and TbYSZ electrodes typically show a higher signal with C<sub>3</sub>H<sub>8</sub> and C<sub>3</sub>H<sub>6</sub> than CO but this is not always the case.

This device was cooled to room temperature, removed from the furnace test stand and transferred to Ford Motor Company. The dynamometer selected utilized a 4.6 liter V8 engine. Given the limitations of the sensor packaging, the sensor was not placed directly in the test manifold; rather it was operated in a separate furnace with an air pump providing exhaust gas taken from the engine manifold. In this configuration, the temperature of the sensor could be precisely controlled. The sensor was exposed to the exhaust gas in a bypass from the main exhaust pipe to ensure proper control of temperature and gas flow. The amounts of HCs and the other constituents in the exhaust gas were varied by changes in catalyst efficiency. The exhaust gas constituents (NO<sub>x</sub>, CO, O<sub>2</sub>, and HCs) were measured using standard dynamometer instrumentation.

Figure 4 shows dynamometer results of a Au/LaMnO<sub>3</sub>/YSZ/Tb-YSZ/Au sensor that utilizes Au current collection as a function of HC concentration as determined by a flame ionization detector (FID). The sensor temperature for this experiment was 620°C; the gas flow through the furnace tube is 1L/min. The measurements were taken during open-loop steady-state engine operation around stoichiometry at 1500 rpm and 50 Nm. The sensor shows a stable EMF response (with no hysteresis) to varying concentrations of total exhaust gas HC content. Also plotted in Figure 4 is the O<sub>2</sub> and CO concentrations measured throughout the run. Figure 5 shows the dynamometer results of the same device operated at 670°C. Again the O<sub>2</sub> and CO concentrations measured throughout the experiment are included. The operating conditions of the dynamometer were nearly

identical. Figure 6 is a plot of the two HC/CO response curves. The decrease in sensor output with increasing temperature is behavior characteristic of mixed potential sensors.

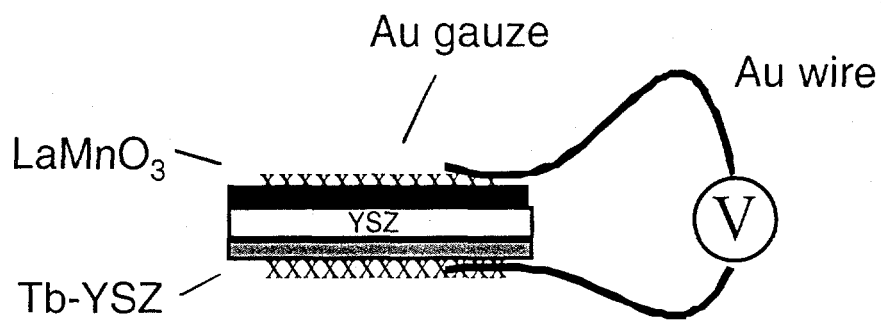
The results of these engine-dynamometer tests are encouraging, although not all our results were as reproducible as the ones shown in Figures 4 to 6. As was reported earlier, mixed potential sensors that rely on Au for the working electrode (i.e. the electrode responsible for generating the mixed potential) show large changes in sensor EMF over time (18). This is caused by a change in the gas-metal-electrolyte triple phase boundary due to recrystallization of the Au electrode at operating temperature. Furthermore, the random formation of the Au triple phase boundary upon initial device operation leads to highly unstable and unpredictable sensor response. Although the mixed potential devices reported here utilize dense metal oxide thin films, the Au used for current collection nevertheless plays a large role in controlling sensor response (18, 19). As such the sensors reported here suffer from similar, albeit to a lesser degree, limitations. The metal oxide materials used in these devices were selected based on their thermodynamic stability and refractory ceramic properties. In order to move forward toward our goal of developing mixed potential sensors that are suitable for automotive applications, we will need to focus on making current collection to the device with out the use of Au or catalytic noble metals.

Another area that needs to be addressed is improved sensor packaging. The packaging scheme used for these experiments permitted easy handling and insertion into the furnace apparatus however repeated thermal cycling would cause the fitting to loosen over time which would cause either loss of electrical contact with the sensor electrodes or would produce noisy or irreproducible signal levels. Another potential problem was chemical reaction between the metal oxide sensor electrodes and the MACOR holder. Portions of the metal oxide electrode that were in contact with the metal oxide electrodes showed evidence of chemical reaction.

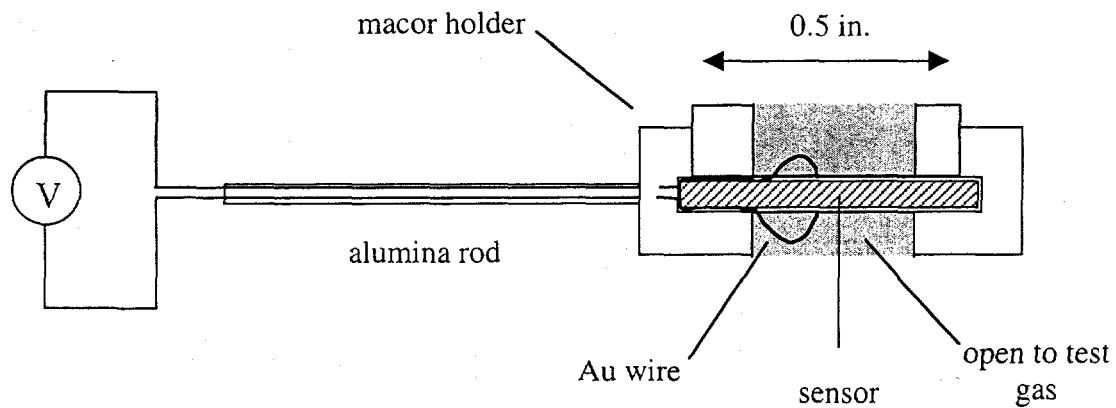
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**Figure 1.** *Aschematic illustration of a mixed potential sensor utilizing metal oxide electrodes (LaMnO<sub>3</sub> and TbYSZ) and Au gauze/ink current collection.*



**Figure 2.** *Sample holder configuration used for this work.*



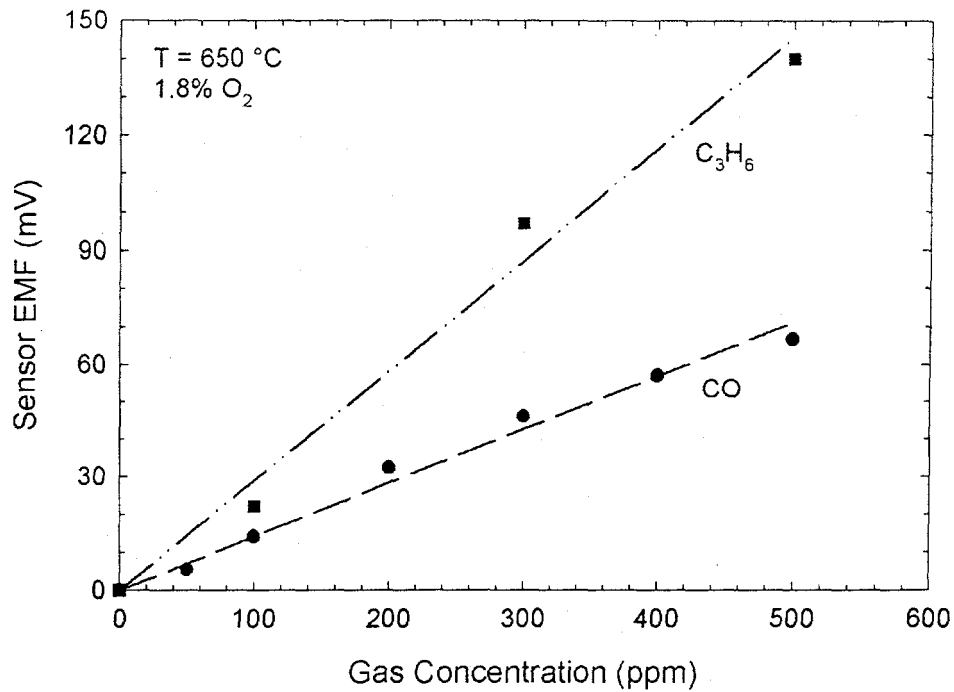


Figure 3. The response of a  $Au/LaMnO_3/YSZ/TbYSZ/Au$  dual metal oxide sensor to  $C_3H_6$  and CO at 650C in 1.8% $O_2$  (balance  $N_2$ ) gas stream.

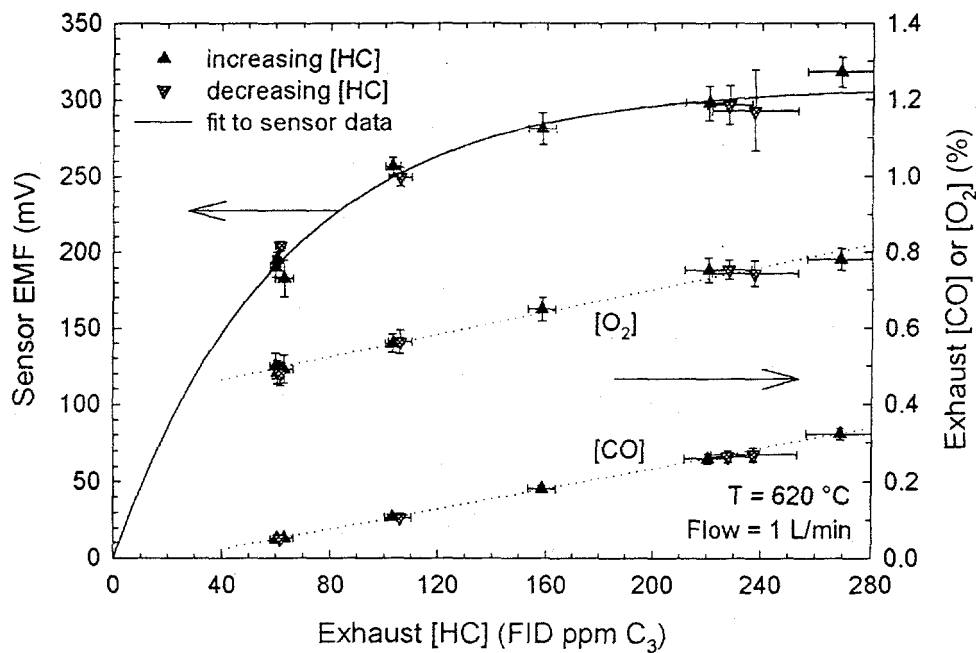


Figure 4. The response of a  $Au/LaMnO_3/YSZ/TbYSZ/Au$  dual metal oxide sensor at 620C exposed to exhaust gas from a 4.6L V8 engine in an engine-dynamometer. The hydrocarbon concentration was determined by FID. The error bars are 6 sigma.