Title: DEVELOPMENT OF CERAMIC MIXED POTENTIAL SENSORS FOR AUTOMOTIVE APPLICATION

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DEVELOPMENT OF CERAMIC MIXED POTENTIAL SENSORS FOR AUTOMOTIVE APPLICATIONS

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Mixed potential sensors that utilize Gd$_{0.2}$Ce$_{0.8}$O$_2$ electrolytes and patterned dense 1 μm-thick LaMnO$_3$ thin films were studied at 600°C and 1%O$_2$. The response to C$_3$H$_6$ and CO of two different sensor configurations were studied continuously for 1000 hrs versus an air reference. Although two different current collection schemes and two different metal oxide electrode geometries were employed, the magnitude of the mixed potential generated by both sensors was remarkably similar. From previous work with Au-ceria-Pt mixed potential sensors, this behavior is attributed to precisely controlling the metal oxide electrode/solid electrolyte interface unlike the random interface produced when Au electrodes are used. Although doped ceria is not a suitable electrolyte for automotive exhaust gas applications, this work serves to illustrate design goals for zirconia-based sensors.
INTRODUCTION

Today's automobiles utilize active closed-loop combustion control of the injected air/fuel mixture together with "three-way" catalysts. A potentiometric zirconia oxygen sensor resides in the exhaust manifold as part of the feedback control system. In multi-cylinder engines, it may be beneficial to use more than one oxygen sensor in order to optimize performance while maintaining optimum efficiency. Stoichiometric engine control allows the three-way catalytic converter to oxidize hydrocarbons (HCs) and CO while simultaneously reducing oxides of nitrogen (NOx). The current generation of low emission vehicles (LEV) is being replaced with ultra-low emission vehicles (ULEV) as required in order to comply with increasingly more stringent emissions standards. However, automobiles with poor-performing or failed three-way catalytic converters are a significant source of air pollution in urban environments. To avoid annual or semi-annual emissions inspections in heavily populated areas, an On-Board Diagnostic (OBD) system has been developed so that the vehicle operator will be alerted in the event the catalytic converter fails.

In the current OBD system, 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 this 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 (1). A direct measurement of the concentration of hydrocarbons may result in a better OBD system in future vehicles. Furthermore, lean burn engine technology will require a new OBD system 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, HCs, H₂ and NOₓ (2-15). The competing reactions of oxygen reduction (oxidation) and CO or HC oxidation (reduction) establish the mixed potential at an electrode. The equations [1] and [2] illustrate this:
\[
\frac{1}{2}O_{2(g)} + V_{o^{\cdot\cdot}} + 2e^- = O_o
\]
\[
CO_{(g)} + O_o = CO_{2(g)} + V_{o^{\cdot\cdot}} + 2e^-
\]

In these equations, \(V_{o^{\cdot\cdot}}\) is an oxygen vacancy and \(O_o\) is a lattice oxygen in the electrolyte. Depending on the rates of these competing reactions, a non-equilibrium potential more negative than that predicted from the Nernst equation develops under oxygen rich conditions (2, 3). The magnitude of the mixed potential is a strong function of the electrochemical and catalytic properties of the electrode material (8, 9). Although various research groups have conducted work on mixed potential sensors for almost two decades, commercial sensors have never materialized. The primary reasons for this have been poor device-to-device response reproducibility, device aging, short lifetimes, and poor selectivity (17, 18).

Williams et al. (4) reported the first mixed potential sensor utilizing an yttria-stabilized zirconia electrolyte with gold and platinum metal electrodes. They reported that the “Pt/YSZ/Au” sensor developed an EMF in the presence of CO and H₂ at temperatures less than 500°C; there was negligible sensor response above this temperature. The response time of a zirconia-based sensor is greatly dependent on its operating temperature. Because of this, it would be useful to operate these sensors at higher temperatures in order to decrease their response times and eliminate the effect of capacitive charging (4). Also, a wide operating temperature range is particularly desirable for automotive applications where exhaust gas temperatures depend on operating and engine load conditions. Higher operating temperatures would also permit greater design flexibility of the exhaust gas system. The exhaust system environment is particularly harsh. Any sensor technology which functions in the exhaust of an internal combustion engine must be able to operate under a wide range of oxygen concentrations and must possess sufficient mechanical, thermal, and chemical stability to operate for at least 100,000 to 150,000 miles or the equivalent of roughly 2000-3000 hours of operation. This would be a tremendous challenge for Au-Pt type mixed potential devices.
Experimentation on Pt/Zirconia/Au type mixed potential sensors has not lead to commercialization of this type of sensor for air monitoring applications much less for automotive applications. The primary reason for this is that, contrary to mechanisms proposed by Williams et al., oxygen reduction kinetics of an electrode are as important as the CO/hydrocarbon oxidation kinetics in determining the mixed potential of that electrode (4). These recently proposed models suggest that the steady-state current is determined by the amount of electrochemical oxidation of the reducing gas and would be decreased by any non-electrochemical oxidation due to the catalytic activity of the electrode or surrounding high temperature environment (e.g. furnace tube surface, sensor packaging, etc.)

The Au electrode used in Pt/Zirconia/Au type mixed potential sensors would re-crystallize and coarsen at elevated temperatures (T>500°C) which would cause a change in the triple phase boundary over time (18). Au electrodes on YSZ exhibit large changes in overpotential with minute changes in steady state current. Therefore, as the Au electrode ages, the change in the oxygen reduction current affects the Au/zirconia interface potential and therefore the mixed potential (17, 18). It is for this same reason that the response characteristics between identically prepared Pt/Zirconia/Au type devices can differ substantially. Since much of the stability problems of mixed potential sensors are caused by the change in the morphology of the noble metal electrodes, the first step toward achieving improved mixed potential devices is to replace the noble metal electrodes with materials that possess the prerequisite mechanical, thermal, and chemical stability.

Improved sensor response stability and reproducibility were observed with these Au-ceria-Pt devices (17, 18). Unfortunately, devices using doped ceria electrolyte cannot be used for automotive applications primarily due to mechanical instability of the electrolyte upon reduction in rich-burn conditions and the subsequent reoxidation of the electrolyte during lean-burn conditions. Also, the Au electrode would still coarsen via recrystallization during high temperature excursions that
inevitably arise during varying engine load conditions. These devices are more suitable for lean-burn combustion control applications such as in gas-fired furnaces.

Until now, attempts to replace the Au and Pt noble-metal electrodes with ceramic, mixed electronic/ionic conductors has not been entirely successful. Initial work focused on dense, 2500Å thick LaSrCoO and LaCoO electrode-based sensors that utilized 5000Å thick sputtered Au films as counter electrodes (19). However, as with Au-zirconia-Pt devices previously reported in the literature, the response behavior reproducibility from device to device was dependent on the Au morphology of the counter electrode and this morphology could vary significantly between samples process with identical thermal treatments. The changing Au morphology on both the Au counter electrode and the Au current collector on the metal oxide electrode were responsible for sensor aging and changes in device response over time.

Extensive testing by Ford Research Laboratory clearly showed drift in sensor response over time along with hysteresis in device response upon cycling PO2 between rich burn and lean burn conditions. It was hypothesized that the hysteresis may have been caused by a change in the oxidation state of the cobaltate film. Although no discernible change could be measured in the lanthanum cobaltate film (based on XRD), the suitability of this material for engine-out conditions was therefore called into question.

Mixed potential sensors that utilized two different metal oxide electrodes were studied next. A comprehensive summary of this work, including actual testing in the exhaust gas of an engine/dynamometer is the focus another publication (20, 21). Au metalization was used for current collection on two dissimilar metal oxides: Tb-doped YSZ and LaMnO3. By using a three terminal electrode configuration versus an air reference, the mixed potential generated on each electrode could be quantified. For example, Figure 1 is a plot of mixed potential as a function of CO concentration in a 1%O2/N2 background gas stream for LaMnO3 thin film electrodes with Pt and Au current collection. Figure 1 shows to what extent the metalization on the surface of the metal oxide...
electrode dictates the magnitude of the mixed potential generated on the electrode regardless of the underlying metal oxide. Also, as with a Pt-zirconia-Au sensors, the Au current collector leads to a mixed potential response that is nonselective to HCs and CO. This can be seen from Figure 2.

In this work, we present recent work on our attempts to engineer new metal oxide-based mixed potential sensor electrodes that do not use Au or Pt metalization on the surface of the metal oxide for the purposes of current collection. The effects on magnitude of the mixed potential and sensor response stability of two different electrode configurations will be presented.

**Experimental**

Gd$_{0.2}$Ce$_{0.8}$O$_{2.3}$ in rod form (0.5” dia. x 1.0” length) was obtained from Praxair. Several 1.0mm thick substrates were cut from this rod stock using a diamond saw. Substrates were cleaned and then mounted onto a Ni faceplate of a sputter system heater assembly using silver-based epoxy obtained from Aremco. The Ni heater faceplate temperature was monitored using a thermocouple embedded within the faceplate. The heater assembly was placed into an ultra-high vacuum sputter system. Depositions were made using on-axis radio frequency (RF) magnetron sputtering technique from a single 2-in. powder target of LaMnO$_3$ (LMO). The LMO target powder was made using standard solid state reaction techniques. Following x-ray diffraction characterization, the LMO powder was packed into 2-in. diameter copper sputter cups to a depth of 0.125 and mounted into the sputter gun in the same manner as a hard target. The sputter conditions were on axis, 600°, a chamber pressure of 40 mTorr of Ar, and a RF power of 100 watts. The deposition time was on the order of 8 hrs. The thickness of the films was measured using a masked sapphire witness sample and subsequent use of a stylus profilometer (DEKTAK). The typical thickness of the metal oxide films was between 1 and 1.2μm.

Two different sensor configurations were explored in this work. In the first configuration, Figure 3, an alumina mask with a 5mm laser-cut square was placed over the GCO substrate prior to
sputtering. The purpose of this was to pattern a square LMO film with a well-defined three-phase boundary on top of the substrate. In the second configuration, a Pt ring electrode was first sputtered onto a GCO substrate (Perkin-Elmer metalization system). A round alumina mask was then used to sputter a LMO film onto the substrate. Part of the LMO film covered the Pt ring electrode (see Figure 4). A small circle of the LMO film was subsequently removed using an Ar ion mill.

A 5000Å-thick Pt reference electrode was sputtered onto the backside of both sensor configurations. The sensor shown in Figure 3 had the final step of the application of a small (3x3 mm), 5000Å thick sputtered Pt current collect or top of the metal oxide.

A Siemens D5000 x-ray diffractometer using CuKα radiation and incident beam monochromator was used to determine the crystal structure, phase purity and lattice parameters of the metal oxide films. Gas mixing was carried out using analog MKS flow controllers. A 1% O2/99% N2 gas mixture flowing at 300 sccm was used as a base gas. A Keithley 236 source measurement unit was used to measure open-circuit potentials of the sensor during testing. The instrument positive lead was connected to the reference electrode and the instrument negative lead as connected to the LMO electrode.

Results and Discussion

In order to eliminate the confusing situation of generating a mixed potential on the counter electrode, a three terminal configuration was selected for this work. The sensor configuration shown in Figure 3 was attached to the end of an alumina tube using Aremco 617 glass. Prior to this step, 0.010” diameter Pt wire was attached to the small Pt pad using a parallel gap wire-bounder. A small amount of the Aremco glass was applied over the Pt current collector. This was done in order to encapsulate the Pt current collector so that it could not participate in electrochemical and non-electrochemical reactions. On the edge of the metal oxide electrode as in contacted the surface of the
solid electrolyte would participate in the electrochemical reactions. The glass was subsequently melted at 900 to 1000°C in an open furnace.

The sensor of the second configuration, Figure 4, was sealed to the end of an alumina tube using Aremco CeramaBond ceramic seal. The CeramaBond was applied such that the Pt ring was not exposed to the gas stream. A 0.010” diameter Pt wire was wire bonded prior to the application of the CeramaBond. CeramaBond is slightly porous, however if applied in sufficient quantity makes for an adequate seal. The advantage of using this cement is that it sets at low temperature and therefore the high temperature anneal of the sensor is avoided.

Figure 5 shows the EMF generated by the addition of C₃H₆ and CO to a base gas stream that contains 1%/O₂/N₂ balance. Stepwise, the concentrations are 0, 50, 100, 300, and 500 ppm. Because there was no oxygen in the C₃H₆ and CO test streams, there was a slight dilution of the O₂ in the base gas stream when C₃H₆ and CO were added. To gauge the effect of this dilution, the experiment was repeated with N₂ only. The EMF change associated with dilution is also shown in Figure 5. The baseline EMF due to the 1%O₂ versus an air reference is not the value calculated from the Nernst equation. This is because of the presence of small leaks most likely due to cracks in the glass seal. In previous work, we found that small leaks in the glass seal does not affect the measurement of the mixed potential (18). The effect of removing the participation of the Pt current collector is immediate: there is a significant decrease in the mixed potential from the CO as compared to the C₃H₆ response. This property is highly desirable from an automotive applications point of view. In OBD-II, CO is considered an interference gas.

The response stability to C₃H₆ and CO was studied over a 1000 hr period of time. These data are shown in Figures 6 and 7. During this time period, the temperature of the sensor was maintained at 600°C. The most significant aging in the C₃H₆ response occurs at higher concentrations. There is negligible change at the 50 and 100 ppm levels of C₃H₆. After 300 hrs, the amount of subsequent change in the C₃H₆ response over time is minute compared to Au-Pt devices (18). The change in the
CO response is also negligible but more importantly, does not increase over time. Figure 8 is a plot of the EMF data versus C\textsubscript{3}H\textsubscript{6} and CO concentration after the 300 hour mark. The error bars reflect the spread of the levels during the experiment.

A second configuration, one more suitable to packaging, was created and tested to see the EMF levels could be reproduced using another device with similar metal oxide/solid electrolyte three-phase boundary length but with an entirely different current collection scheme. Presumably, if the amount of heterogeneous catalysis is similar between devices, the EMF levels for a given C\textsubscript{3}H\textsubscript{6} and CO concentration should be the same. Figure 9 shows the initial response to N\textsubscript{2}, CO, and C\textsubscript{3}H\textsubscript{6} a short time after the furnace stabilized at 600°C. Stepwise, the concentrations are 0, 50, 100, 300, and 500 ppm. Recall that this device has never been annealed above 600°C temperature that the LMO film was sputtered. The CO EMF is larger than the previous configuration but more interestingly, the C\textsubscript{3}H\textsubscript{6} EMF is much larger and a small amount of hysteresis is seen upon reducing C\textsubscript{3}H\textsubscript{6} levels back to zero.

This sensor was left at 600°C for 1000 hrs and the response to CO and C\textsubscript{3}H\textsubscript{6} was periodically measured in the same manner as the previous device. Figure 10 shows the C\textsubscript{3}H\textsubscript{6} response over the entire 1050 hrs of testing. The baseline EMF (i.e. the EMF versus air reference for 1%O\textsubscript{2} in the base gas stream) was subtracted from the curves because it exhibited a small upward drift over time as the CeramaBond seal improved with annealing time. There is a large change in EMF level with time only at the 300 and 500 ppm levels; the most significant change occurs at the 500 ppm level. After 500 hrs, whatever changes were occurring in the electrode morphology appear to cease. Only the 500 ppm level has not fully stabilized with respect to time. The reason for the aging effect in this device has not been determined. However, it is interesting to compare both devices after their extended anneals. Figure 11 follows the CO EMF levels during this experiment. This shows a decrease in the CO response although it is not as large a change as compared to propylene.
Figure 12 is a plot of mixed potential (i.e. the potential above the equilibrium EMF after complete combustion of C$_3$H$_6$ or CO) for both devices at 600°C and in 1%O$_2$. Remarkably, both sensor configurations produce very similar mixed potential levels. Two Au-Pt devices prepared and annealed in an identical fashion would not produce mixed potential values this close to one another (17-19). Unlike previous work, these data show that the mixed potential generated is independent and unaffected of the current collection scheme. Also, by producing two devices with similar metal oxide/solid electrolyte line length, the magnitude of the mixed potential is similar. This is extremely important from an automobile sensor manufacturer’s point of view.

Mukundan et al. found that Au-Pt mixed potential sensors made using doped ceria electrolytes produced similar responses if the Au and Pt electrodes were not first annealed. Annealing would invariably cause recrystallization and grain growth and thus an increase in the triple phase boundary between the Au and solid electrolyte. Without recrystallization, the electrochemical oxidation and reduction reactions occur on the well-defined edge between the Au film and the solid electrolyte. The data presented in this paper suggests that the dense, metal oxide LMO electrode is acting like the Au metal electrode only with different electrocatalytic and heterogeneous catalytic properties. The resistance to aging over time is a reflection of the refractory nature of the metal oxide electrode. Different metal oxide electrode materials can now be studied and the effects of the heterogeneous catalysis properties on the magnitude of the mixed potential can be studied.

As stated before, doped ceria was used to compare these data with past work. Ceria substrates do not possess the prerequisite mechanical and thermodynamic stability to be used in an automobile exhaust environment. Engine/dynamometer testing of sensors that use zirconia electrolyte with controlled electrode interfaces will therefore be the focus of future work.

**Conclusions**

We have demonstrated a reproducible mixed potential response versus an air reference electrode by using a patterned LaMnO$_3$ film to control metal oxide electrode/solid electrolyte interfacial
properties. Two different current collection schemes were explored. Both methods produce similar mixed potential behavior. The removal of the Pt current collector from participating in the electrochemical reactions appears to be a crucial step to making reproducible and stable mixed potential sensors that utilize metal oxide electrodes. Additionally, the removal of the heterogeneous catalysis properties of the Pt current collector make the sensor configuration less sensitive to CO. The findings of this work will be applied to investigating patterned metal oxide electrodes on zirconia electrolytes. Although response time was not studied in this work, the 10-30 sec response time that these devices exhibit remains the major impediment for use as automotive OBD sensors.

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REFERENCES

1. Ford work


Figure Captions

1. A plot of mixed potential versus CO concentration from 2500Å-thick films of LaMnO₃ with Pt and Au 3x3 mm 5000Å-thick current collection pads sputtered onto the metal oxide. The devices were mounted onto a YSZ tube for 2-terminal measurements against an air reference electrode. The temperature was 600°C in a 1%O₂/N₂ atmosphere.

2. A comparison of the mixed potential generated on a Au/LaMnO₃ electrode versus a Pt/air reference electrode for equivalent concentrations of C₃H₆ and CO. The temperature was 600°C in a 1%O₂/N₂ atmosphere.

3. An illustration of the encapsulated Pt current collector configuration used for the first sensor.

4. An illustration of the buried Pt current collector configuration used for the second sensor.

5. EMF response versus a flowing air reference of the encapsulated Pt pad device shown in Figure 3. Three data sets are shown for CO, N₂ blank, and C₃H₆. The concentration levels are 0, 50, 100, 300, and 500 ppm. The temperature is 600°C in a background of 1%O₂/N₂ balance.

6. The EMF response of the encapsulated Pt pad device to 0, 50, 100, 300, and 500 ppm of C₃H₆ over 1000 hours of continuous operation at 600°C in 1%O₂/N₂ balance.

7. The EMF response of the encapsulated Pt pad device to 0, 50, 100, 300, and 500 ppm of CO over 1000 hours of continuous operation at 600°C in 1%O₂/N₂ balance.
8. The EMF versus a Pt/flowing air reference electrode plotted against CO and C3H6 concentration for the lifetime data presented in Figures 6 and 7 averaged from the data after 300 hrs. The error bars represent the spread of EML levels measured.

9. EMF response versus a flowing air reference of the buried Pt current collector device shown in Figure 4. Three data sets are shown for CO, N2 blank, and C3H6. The concentration levels are 0, 50, 100, 300, and 500 ppm. The temperature is 600°C in a background of 1%O2/N2 balance.

10. The EMF response of the buried Pt current collector device to 0, 50, 100, 300, and 500 ppm of C3H6 over 1000 hours of continuous operation at 600°C in 1%O2/N2 balance.

11. The EMF response of the encapsulated Pt current collector device to 0, 50, 100, 300, and 500 ppm of CO over 1000 hours of continuous operation at 600°C in 1%O2/N2 balance.

12. The mixed potential values calculated from the EMF measurements taken after 1000 hours of continuous 600°C operation for both the encapsulated Pt pad device and buried ring electrode current collector device.
Fig 1
Fig 2
Figure 7

Solids electrolyte

Pt

3-phase boundary

LaMnO$_3$ film

Pt

SE

Pt air ref

Alumina tube

Pt wire

top view

side View

Figure 2
EMF vs Air Reference (mV)

Time (min)

Fig 5
Fig 7
EMF vs Air Reference (mV)

Gas Concentration (ppm)

- $\text{C}_3\text{H}_6$ EMF levels
- CO EMF levels

Figure 8
Fig 9
EMF vs Air Reference (mV)
1% \text{O}_2 baseline subtracted

Time (hrs)

Fig 10
EMF vs Air Reference (mV)
1%O₂ baseline subtracted

Time (hours)

Fig 11

CO response
Fig 12

Graph showing the relationship between gas concentration (ppm) and mixed potential (mV) for different electrodes.