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ABSTRACT

Several types of electrochemical sensors have been studied for application in an automobile. The most prevalent amongst these is the zirconia oxygen sensor, which is also known as the λ -sensor or Exhaust Gas Oxygen (EGO) sensor. This sensor is used to monitor the oxygen partial pressure in the exhaust, which in turn is utilized to control the air/fuel ratio to the engine. Currently, two such oxygen sensors are being used to determine the "state-of-health" of the catalyst. One sensor is placed upstream of the catalyst and another downstream, and the catalyst efficiency is indirectly monitored by measuring its' oxygen storage capacity. However such a system has several disadvantages and works only when the engine is operated around stoichiometry. There is increasing interest in developing a hydrocarbon sensor that can be used directly to measure the amount of non-methane hydrocarbons (NMHC) in the exhaust stream. The results of a newly developed mixed-potential sensor using platinum (Pt) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ -oxide (LSCO) electrodes on a 8m% yttria stabilized zirconia (YSZ) electrolyte are presented and its potential application as an automotive NMHC sensor is discussed. This sensor has a response of 40 mV to 500 ppm of propylene at 773K in 1% O_2 while the response to the same amount of CO is only 2 mV.

INTRODUCTION

Tailpipe emissions from automobiles are under increasing scrutiny of the Environmental Protection Agency (EPA) and California Air Resource Board (CARB). California exhaust emission standards for all 2001 model year passenger cars mandates that the non methane organic gasses (NMOG) coming out of the tailpipe of Tier 1 and LEV vehicles be less than 0.25 and 0.075 g/mile (1.55×10^{-4} and 4.66×10^{-5} g/m) respectively. Moreover the EPA and CARB also

require manufacturers to comply with On-Board Diagnostic (OBD-II) requirements, which mandate that the automobile user be warned by a Malfunction Indicator Light (MIL) when the tailpipe emissions increase by 0.4 g/mile (2.5×10^{-4} g/m). These requirements are currently being met by the dual EGO sensor technology.^{1,2}

The dual EGO sensor consists of two **Heated-EGO** (HEGO) sensors, one placed up-stream of the catalyst and the other down-stream. The up-stream sensor monitors the oxygen partial pressure in the exhaust gases before the catalytic convertor and is used to adjust the Air/Fuel (A/F) ratio to the engine. If the engine is run around stoichiometry, then this sensor displays a step-like response when the A/F ratio changes from rich to lean and vice-versa.³ However, the response of the second sensor (down-stream of the catalyst) is either delayed and/or dampened due to the oxygen storage capacity of the convertor. The precious metals and the ceria-washcoat in the catalyst have a tendency to store oxygen, which is consumed during hydrocarbon (HC) oxidation and replenished during nitrogen oxide (NO_x) reduction. This oxygen storage capacity (OSC) can be linked to the HC conversion efficiency of the catalyst and is found to have a step like relationship where the OSC decreases dramatically when the HC conversion efficiency drops from around 95% to 80%. Therefore the ratio of the two sensor responses can be used as an indirect measure of the hydrocarbon conversion efficiency of the catalyst.^{1,2}

Although this dual oxygen sensor approach has worked successfully, there are several disadvantages to this dual EGO sensor approach because it is not a direct measure of the HC conversion efficiency of the catalyst. The ratio of the responses of the two HEGO sensors is very sensitive to the HC conversion efficiency when the efficiency is > 80%. However, this measure is insensitive when the HC conversion efficiency drops below 70%.¹ Hence this method tends to classify catalysts that are working at 60-75% efficiency as “failed catalysts”. Moreover, in order for this technology to work, the engine should be operated in the closed loop fuel control mode that results in the oscillations of the A/F ratio around stoichiometry. These problems can be greatly alleviated by the development of a sensor that would directly measure the HC content before and after the catalyst.

One such technology that has the potential to measure HCs in a background of O₂, N₂, H₂O, CO₂, CO and NO_x is the mixed-potential sensor.^{4,5} Mixed potential sensors have been used in the past for the detection of CO^{6,7}, NO_x⁸, H₂⁹ and HCs.¹⁰ These sensors rely on the fact that two dissimilar electrodes on an oxygen-ion conducting electrolyte exhibit different non-equilibrium potentials in the presence of a reducing gas and oxygen. The potential at any one electrode is fixed by the rate of electrochemical oxidation of the reducing gas (CO, HC's or NO₂) and the rate of electrochemical reduction of oxygen (Eqns. 1 & 2).⁴

The factors that determine the mixed-potential at an electrode/electrolyte interface include; the electrode material, electrode surface-area, 3-phase interface length, amount of reducing gas and oxygen present, flow rates of the gases, and temperature of the measurement.¹¹ The working principle of a mixed potential sensor operating at 773-873 K in a 1%O₂ stream with 0-500 ppm of reducing gas was recently illustrated using a four electrode “Pt/Ce_{0.8}Gd_{0.2}O_{1.9}/Au” sensor consisting of Pt and Au sensing electrodes and 2 corresponding Pt reference electrodes.¹² It was found that the steady state current was determined primarily by the amount of electrochemical oxidation of the reducing-gas while the voltage was determined primarily by the oxygen reduction kinetics of the Au electrode. The response of this sensor to various gases is illustrated in Figure 1 while the stability of response of the individual Au and Pt electrodes is represented in Figure 2.¹² Figure 1 shows that the Au electrode has very little selectivity to HCs relative to CO and H₂. Moreover, from Figure 2 it is clear that the mixed potential is primarily at the Au electrode while the Pt electrode acts like a pseudo-reference electrode and the stability of the Au electrode is less than desirable.

Figure 1. Response of a “Pt/Ce_{0.8}Gd_{0.2}O_{1.9}/Au” sensor to various reducing-gases at 873 K. Reproduced by permission of The Electrochemical Society, Inc.¹²

Figure 2. Stability of the gold and platinum electrode potentials to CO in a 1%O₂ stream at 873 K. Reproduced by permission of The Electrochemical Society, Inc.¹²

Recently, there have been several publications trying to address these limitations by replacing the Au electrode with an oxide or composite electrode. The electrode materials that have been reported include Au-10%Ta₂O₅¹⁰, In₂O₃-0.1%MnO₂,¹³ and CdO.¹⁴ In this paper we report the response of a La_{0.8}Sr_{0.2}CrO₃ (LSCO) electrode on a YSZ electrolyte.

EXPERIMENTAL

The sensor consists of a LSCO electrode, a Pt electrode and a YSZ electrolyte. The LSCO electrode was prepared from La_{0.8}Sr_{0.2}CrO₃ powders from Praxair®. The powders were first uniaxially pressed in a 1.9 cm die at 15 Mpa for 300 s and then isostatically pressed at 200 MPa for 300 s. The LSCO samples were then sintered at 1923 K for 36000 s and pellets of approximately 2x2x2 mm³ were cut from this ceramic to be used as the LSCO electrode. A LSCO pellet and a Pt wire (dia. = 0.25 mm) were then placed on a 1.9 cm die and covered with 3 gms of YSZ powder. This was then pressed at 23 Mpa for 300 s and the resulting sensor assembly was sintered at 1273 K for 36000 s.¹⁵ Two identical sensors (sensor #1 and sensor #2) were prepared using the above technique.

The sensor was then mounted on an alumina rod with Pt leads which was then placed in a quartz tube and heated in a furnace to the operating temperature. The flow rates of the various gas mixtures were controlled using automatic MKS mass flow controllers while the voltage from the sensor was monitored using a Keithly 2400 Source Measure Unit (SMU). The data acquisition was performed using Labview® software running on an Apple® computer. The base gas used was 1%O₂/N₂ which was flown at $3\text{--}5 \times 10^{-3}$ L/s over the sample. The mix gases used were 2500ppm Propylene/N₂, 2500 ppm CO/N₂, 2500 ppm Propane/N₂, 1000 ppm H₂/N₂, and 2500 ppm Methane/N₂. The flow rate of the mix gas was adjusted so as to give the appropriate concentration of the sensing gas in the test mixture.

RESULTS AND DISCUSSIONS

The response of the two sensors to varying concentrations of propylene in a base gas of 3.3×10^{-3} L/s (200 cc/min) of 1%O₂/N₂ is shown in Figure 3. The initial response of sensor #1 was much lower than that of sensor #2. However, when both sensors were annealed at 1073 K for 3600 s, their responses were almost identical. Moreover, it is seen from Figure 3 that there is no change in the response of sensor #2 to the annealing process. The Pt electrodes of sensor #2 (unlike sensor #1) were cleaned before they were incorporated into the sensor, indicating that the annealing process cleans up the surfaces of the electrodes from

Figure 3. Response of Sensor #1 and #2 to varying concentrations of propylene in a 1%O₂ background at T = 773 K.

Figure 4. Stability of the response of sensor #1 to varying concentrations of propylene in a 1%O₂ base gas at 773 K.

Figure 5. Stability of the response of sensor #2 to varying concentrations of propylene in a 1%O₂ base gas at 823 K.

any adsorbed contaminants. The sensor to sensor reproducibility of these two sensors was within 20% for 50 ppm of propylene and within 1% for 500 ppm of propylene. This reproducibility is attributed to the precise control of the electrode morphology achieved by using a ceramic pellet instead of a sputtered or painted-on gold electrode.^{16,17}

Figures 4 and 5 illustrate the stability of the propylene response of sensor #1 and #2 at 773 K and 823 K respectively. The response curves indicate that these sensors are very stable at both these temperatures for up to 10 days. The stability of these sensors is a result of the stable morphology of the ceramic-pellet electrode, which does not coarsen with time. This is in contrast to the stability of the Au electrode (Figure 2) whose morphology does change with time due to the re-crystallization of the Au film.¹²

The response time to 90% of signal level of these sensors is < 25 s at 823 K and < 35 s at 773 K. Although the data points were taken every 2-4 s, only 5% of the data points are shown in the figures for clarity. The response time of these sensors is expected to be a function of the kinetics of the oxidation and reduction reactions (Eqns. 1 & 2) occurring at the two electrodes. However the specific factors that control the kinetics of these reactions are not clearly understood at this time and need to be addressed in detail.

Figure 6 illustrates the response of sensor #2 to various gases at 823 K. In this experiment the base gas (1%O₂/N₂) flow was kept constant at 3.3×10^{-3} L/s (200cc/min) and the mix gas (containing no oxygen) flow was slowly increased from 3.7×10^{-4} L/s to 3.3×10^{-3} L/s. Hence the oxygen partial pressure is not

Figure 6. Response of sensor #2 to various gases at 823 K.

constant and varies from 1%O₂ at 0 ppm of mix gas to 0.5%O₂ at 1250 ppm of mix gas. The sensor response has a linear relationship to the concentration of all the gases, while the response to the hydrocarbons (Propylene and Propane) is ≈ 14 times that of CO. Moreover the sensor has only a slightly negative response to H₂ and methane which is probably due to a small mixed-potential on the “pseudo-reference” platinum electrode. This is in contrast to the gold-electrode-based sensor, which has almost no selectivity towards the hydrocarbons (Figure 1).

It is worth mentioning that in Figure 6, the data point for 1250 ppm of propane does not lie on the linear response curve but is actually lower than the response for 1000 ppm of propane. As mentioned earlier, the oxygen concentration was not kept constant in this experiment and for this particular data point was at 0.5%O₂. Hence when 1250 ppm of propane is present alongside 5000 ppm of O₂, we have (see equation 3) crossed over from the lean side to the rich side of stoichiometry.

Hence these sensors have a linear response curve to the concentration of reducing-gas only in the presence of excess oxygen. Thus these sensors can be operated only on the lean side of stoichiometry and probably would not work for an engine that is running fuel rich.

CONCLUSIONS

The newly fabricated “LSCO/YSZ/Pt” sensor has several desirable characteristics that could be utilized in an on-board hydrocarbon sensor for monitoring automobile tailpipe emissions. The sensor has good selectivity to hydrocarbons and excellent stability and reproducibility. The long-term stability of these sensors and their ability to withstand the harsh conditions in an automobile exhaust needs to be examined. However, these can be expected to be reasonably good considering the stability of the individual components used. The YSZ electrolyte is currently being used in the EGO sensor and the platinum electrode should be at least as stable as the platinum used in the catalytic converter. Moreover, the other electrode (LSCO) is currently being considered as an interconnect material in solid oxide fuel cells and is known to withstand high temperatures (up to 1273 K) and huge swings in the partial pressure of oxygen. However, the response time (< 25 s to 90% of response at 823 K) and sensitivity (≈ 2.5 μ V/ppm of propylene at 823 K and 1%O₂) of this device are still major impediments to the practical application of these sensors.

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