Non-Nernstian potentiometric sensors based on YSZ for high temperature applications

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Strict norms on pollution control are being enforced worldwide, especially for what concerns emissions of vehicles (1). To control and reduce automobile emissions, the On-Board Diagnostic (OBD) system has been introduced to control the main pollutants, such as NO_x, HCs and CO. The OBD is a complex, closed-loop system to continuously monitor the pollutant concentrations in the exhausts. At present, given the lack of reliable CO/hydrocarbons and NO_x sensors, OBD is performed using oxygen sensors. Solid oxide electrochemical O_2 sensors are inexpensive and have successfully shown to work in harsh combustion exhaust environment. If modified to selectivity measure NO_x or CO /hydrocarbons concentrations, this type of sensors can be used to improve the combustion as a feed-back elements in engine control systems.

Planar sensors based on tape-cast YSZ layers (150 μm of thickness) were fabricated. Two Pt finger electrodes were deposited on one side of the layers. One of the electrodes was covered with an oxide thick film. Two different oxides were tested, WO_3 which is a n type-semiconductor and $La_xSr_{1-x}FeO_3$ which is a mixed ionic-electronic conductor. The oxides were prepared in the laboratory using different chemical routes. Previous works refer to WO_3 sensors prepared by using commercial WO_3 powders (2, 3). The oxide powders were mixed with a screen-printing oil and thus painted on one metallic electrode. Scanning electron microscopy (SEM) investigation showed nano-sized grains for the oxide powders.

The sensors were tested in potentiometric devices at various concentrations of NO_2 and CO (200-1000 ppm in synthetic air), at different temperatures in the range 500-650°C. The sensing mechanism of the sensors has been also investigated (4) and the influence of the oxygen partial pressure on the sensors performances was also studied. For both WO_3- and $La_xSr_{1-x}FeO_3$-based sensors a linear correlation was observed between the EMF values and the NO_2 and CO concentrations in logarithmic scale. The EMF response was in opposite direction upon exposure to NO_2 and CO and opposite for the two sensors. The amplitude of EMF signal at a fixed gas concentration was measured at different oxygen partial pressures and increased with decreasing oxygen in the atmosphere.

Some electromotive force (EMF) measurements were also performed in an engine bench test. Planar sensors were located close to a commercial oxygen sensor, downstream the three-way catalytic converter of a FIAT fire 1242 c.c. spark ignition engine coupled to a dynamometer. The gas sensor packaging used was like a commercial lambda probe provided with heating facility. Another commercial oxygen sensor was located upstream the catalytic converter to control the air/fuel ratio (A/F) of the engine. EMF response of gas and oxygen sensors both located downstream the catalytic converter were recorded simultaneously. The performance of the gas sensors was measured at the stoichiometric point (A/F=14) at different engine regimes (RPM and torque) and thus at different operating temperatures. The EMF measurements were related to the exhaust gas concentrations measured by spectroscopic analytical equipment at the engine exhaust end.The engine was switched off and started up many times in different operating conditions to study the response time, the reproducibility, and the stability of the gas sensor.

Figure 1 shows the signal output (EMF) of the WO_3 planar sensor compared to that of the commercial lambda probe both positioned in the engine bench. During the test the engine regime was about 3000 round/min and the torque was changed in order to have high or low CO concentrations in the exhausts. Three peaks (A, B, C) have been measured by setting the engine parameter to have approximately the same high CO partial pressure in the exhausts. The temperature measured close to the gas sensor and the lambda probe was about 695°C.

To increase the NO_x concentration in the exhausts, some measurements at lean-fuel conditions (A/F>14) were also performed.

Preliminary measurements showed promising results in terms of sensitivity, stability and reproducibility, and a reasonably fast response time.

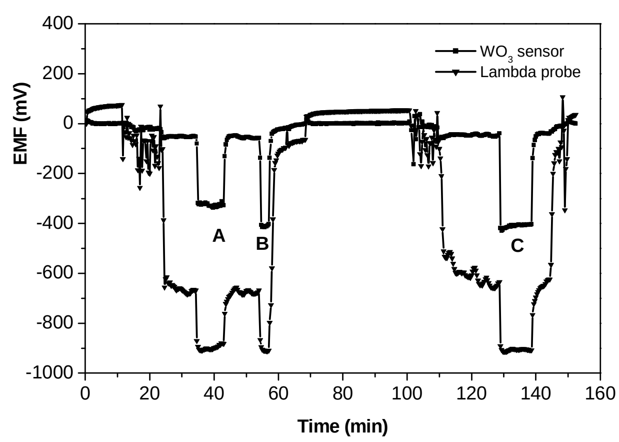

Figure 1. *EMF of the WO_3 planar sensor compared to that of the commercial lambda probe in the engine bench.*

References

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