Thin Film Mixed Potential NO_x Sensor Development for Stationary Reciprocating Engine Applications

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Advanced reciprocating engines require new sensor technologies to reduce emissions and to improve overall combustion efficiency. Engine feedback control, NO_x emissions monitoring and control, and sensors to control the regeneration of reduction catalysts are required. Some of the principal goals of the DOE's Advanced Reciprocating Engine System (ARES) program are to improve fuel efficiency and flexibility, and reduce emissions of engine systems used for distributed energy generation applications. The NO_x emissions target for natural gas-fired reciprocating engines is 0.1 g/bhp-hr (roughly a factor of ten reduction from current levels). A new NO_x sensing technology is necessary to meet the sensor requirements for low cost, sulfur tolerance, and a long, stable lifetime. The sensors developed over the last decade for lean-burn gasoline engines cannot meet all of these requirements. In our past work, we have developed CO and HC mixed potential sensors based on doped zirconia [1-3] and ceria [4] electrolytes and metal oxide electrodes for automotive on-board diagnostic applications. We are presently engaged in work to determine whether our sensors would be suitable for NO_x sensing and combustion control in large, natural gas fired reciprocating engines.

Mixed potential sensors based on Mg and Sr-doped lanthanum chromite and Pt electrodes with thin film, YSZ solid electrolyte are studied for NO/NO_2 sensitivity, CO/CH_4/HC cross sensitivity, and voltage level stability in this work. Thin films of $La_{0.8}(Sr,Mg)_{0.2}CrO_3$ and $LaCr_{0.8}Mg_{0.2}O_3$ were prepared using RF magnetron sputtering via a mixed phase, fluoride precursor route [5]. Thin films of YSZ electrolyte (< 15µm) were prepared using e^- beam evaporation. Planar sensor configurations were selected to facilitate the future incorporation of a thin film heater.

Figure 1 is the initial sensor response to NO_2 at 650°C in a base atmosphere of 10.4% O_2. The device response showed a fast response time with excellent reproducibility in the voltage levels with changing NO_2 concentrations. The temperature was lowered to 600°C with little change in the NO_2 level (small temperature coefficient) as can be seen from Figure 2. Figure 2 shows the cross sensitivity to CO and to a few selected HCs; particular attention was made to the cross sensitivity to CH_4. The aging effects were also studied for NO_2 (Figure 3) along with NO, CO, C_3H_6, C_3H_8, and CH_4. In addition, the PO_2 dependence was studied as well for this sensor.

Initial experiments have also been performed to demonstrate the use of pre-catalysts to enhance selectivity. Multi-electrode devices and the use of pre-catalysts were studied as potential methods to mitigate cross sensitivity to non-methane HCs and CO as well as to control NO/NO_2 selectivity at different temperatures. We will also present in this talk some preliminary work in the exploration of doped fluorite and spinel metal oxide thin films as potential NO_x-specific working electrodes for mixed potential sensors.

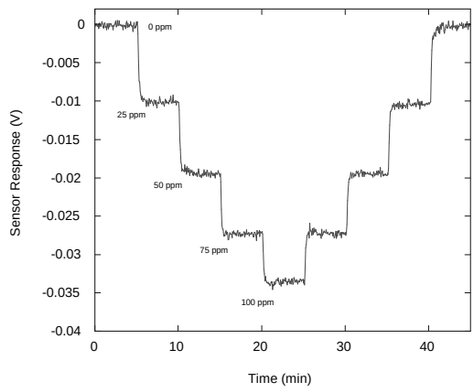

Figure 1. Initial NO_2 response, 0-100 ppm, at 650°C, 10.4 % O_2/N_2 balance flowing at a base flow rate of 500 SCCM.

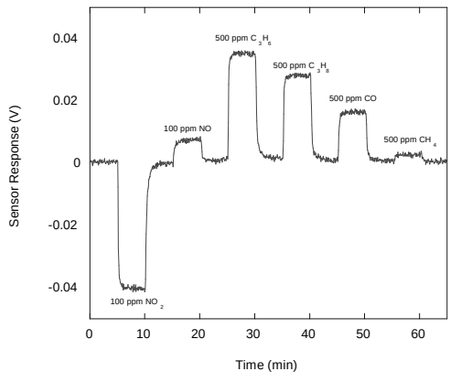

Figure 2: Cross sensitivity studies: sensor response to NO_2, NO, and selected HC's and CO versus time at 600°C. Base gas is 10.4% O_2 at a flow rate of 500 SCCM.

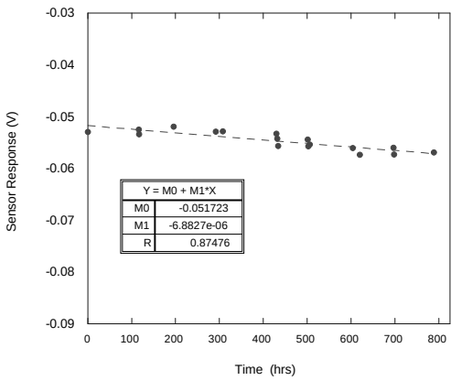

Figure 3: Plot of sensor voltage measured at 100 ppm of NO_2 versus a time period of 800 hours at 600°C in 10.4% O_2.

References:

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