Mixed-Potential NO_x Sensors: Reproducibility Between Devices Prepared by Commercial Manufacturing Methods

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Current regulations are driving the reduction of pollutants emitted from heavy-duty diesel engines. Two commonly employed technologies are selective catalyst reduction (SCR) and exhaust gas recirculation (EGR). These technologies, combined with regenerative particulate traps, have reduced NO_x and tailpipe emissions in diesel vehicles by 95%[1]. Integrating NO_x sensors with these systems would improve their efficiency, provide diagnostics for state of operation, and could be used in an on-board diagnostic scheme for optimizing fuel efficiency under conditions that minimize emitted pollutants. Current NO_x sensing technology involves complex and expensive electrochemical pumping cells. Mixed-potential sensors fabricated via well-established commercial manufacturing methods present a promising alternative to enable the widespread utilization of NO_x sensing technology. The electrochemical devices and sensors group at LANL has worked in collaboration with Electro-Science Laboratories (ESL, King of Prussia, PA) to fabricate mixed-potential NO_x sensors via readily scaled, cost-effective manufacturing methods already employed in the manufacturing of planar O_2 λ-sensors.

The two sides of the planar, self-heated, tape cast sensor prototype are shown in Figure 1. The sensing component consists of screen-printed LSCrO- working and Pt-counter electrodes coated with a porous YSZ electrolyte layer. A Pt-heater with independent leads is printed on the backside of the ceramic substrate. The non-Nernstian "mixed-potential" developed in the presence of a given analyte gas is due to the difference in electrochemical reaction rates occurring at dissimilar electrode/electrolyte interfaces. Employing electrode materials that possess varying electro-catalytic activities towards the redox half reactions has been shown to further increase the mixed-potential response. In the present NO_x sensor, the working electrode, $La_{0.8}Sr_{0.2}CrO_3$ (LSCrO), is known to be a poor catalyst for the oxygen reduction reaction whereas the Pt counter electrode is known to possess high catalytic activity. Operated at open circuit, this combination of electrode materials serves as a sensor for reducing gases, such as hydrocarbons and ammonia. However, the sensor can be transformed to a total NO_x sensor by appropriate tuning of the current bias and operating temperature[2, 3].

Previous work has demonstrated the sensitivity and long-term durability of the planar tape-cast NO_x sensor[4]. The work reported herein considers the reproducibility of the sensor response between multiple devices. An example of device-to-device variability is illustrated in Figure 2 for two different sensors with nominally identical fabrication and macro-scale geometric dimensions. As shown in Figure 2, the unbiased response is very similar for the two devices, but the biased response differs by an approximately 100 mV shift in baseline. This shift in baseline response is indicative of a change in resistance between the two devices. While the macro-scale geometric dimensions are the same, variations in electrode and electrolyte microstructure and three-phase boundary regions may significantly influence device resistance. Electrochemical Impedance Spectroscopy (EIS) is used to probe the electrolyte and interfacial resistances to better understand the root of observed variation in biased sensor response. This work also systematically investigates the influence of varying three-phase regions by fabricating and testing devices with different lengths of the electrodes underneath the porous YSZ electrolyte layer.

In addition to identifying device reproducibility for identically fabricated devices, it is also necessary to assess the tolerance of the device response to common manufacturing variations and/or defects. To that end, we will also report on the performance of devices with pin-hole type defects and non-uniform electrode boundaries.

Figure 1: ESL prototype sensor

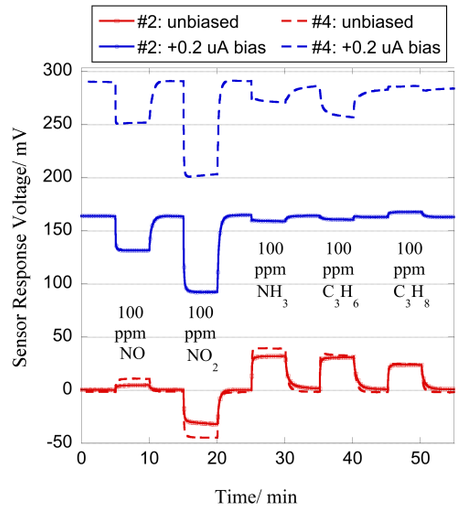

Figure 2: Sensor voltage response of two different devices in varying analyte gas species at 0 bias (red) and +0.2 μA bias (blue).

References

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