

Impedance as a diagnostic tool to characterize mixed-potential sensor response

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Stable, robust and inexpensive NO_x sensors would further enable the development of emission control technologies to realize highly efficient and emission compliant lean-burn gasoline and diesel engines. Mixed-potential sensors fabricated via well-established commercial manufacturing methods present a promising avenue 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 the readily scalable, cost-effective high temperature co-fired ceramic (HTCC) technology already employed in the manufacturing of planar O₂ λ-sensors¹.

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. In contrast to the O₂ λ-sensors where the sensor response is governed by equilibrium thermodynamics, the response of mixed-potential sensors is governed by reaction kinetics and is therefore highly sensitive to both heterogeneous reactions and the electrochemical reactions taking place at the three-phase interface between the gas phase, electrode and electrolyte. Issues surrounding selectivity, stability and reproducibility have hindered the commercialization of mixed-potential sensors.

The two sides of the planar, self-heated, tape cast sensor prototype are shown in Figure 1. The sensing component consists of dense La_{1-x}Sr_xCrO₃ (LSCrO)-working and Pt-counter electrodes coated with a porous YSZ electrolyte layer. The use of dense electrode and porous electrolyte morphologies aids in the stability of the three-phase interface. A Pt-heater with independent leads is printed on the backside of the ceramic substrate. 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 temperature². In this work, we have investigated the influence of varying the embedded electrode length—the length of LSCrO and Pt electrodes covered by the porous YSZ electrode layer. The response to varying NO concentration of two sensors with embedded electrode lengths of 3mm (Sensor 1) and 5mm (Sensor 2) is shown in Figure 2.

The impedance response of each sensor in the base gas of 10% O₂- balance N₂ and with 100ppm NO and NO₂ is shown in Figure 3. The resistance of the YSZ layer extracted from the high frequency response scales with the sensor geometry, and the electrolytes of both sensors possess equivalent conductivities when scaled by their respective geometric surface areas. Somewhat surprisingly, the low frequency impedance response

attributable to the electrochemical processes (ionic diffusion and charge-transfer reactions) does not scale with sensor geometry. In this work, we will use impedance as a diagnostic tool for understanding how sensor geometry influences the rate-limiting electrochemical processes and the measured sensor response.



Figure 1: ESL prototype sensor

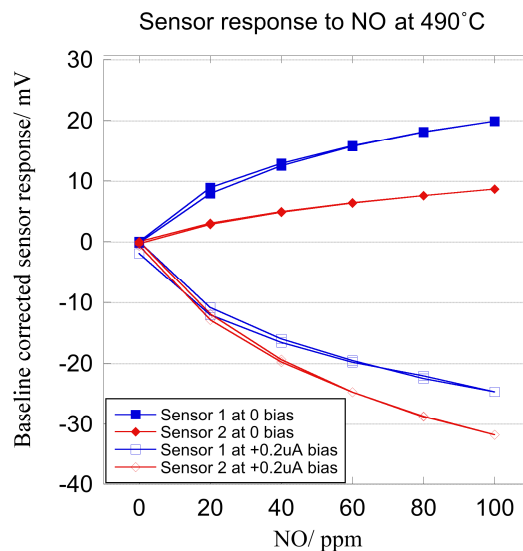


Figure 2: Sensor response to varying concentrations of NO at 0 and +0.2uA bias for 2 sensors with 3mm (sensor 1) and 5mm (Sensor 2) embedded electrode length.

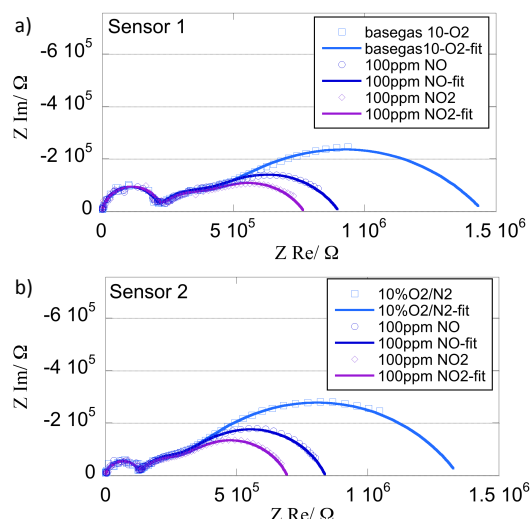


Figure 3: Impedance response at 490°C of a sensor with a) 3mm embedded electrode length and b) 5mm embedded electrode length, in varying analyte gas species in 10% O₂/ balance N₂.

References

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