Quantitative Decoding of Ammonia-Hydrocarbon Mixtures using Zirconia-based Mixed Potential Sensors

Cortney Kreller[1], Julia Tsitron[2], Praveen K. Sekhar[3], Rangachary Mukundan[1], Fernando H. Garzon[1], Alexandre V. Morozov[2], and Eric L. Brosha[1]

[1]*Los Alamos National Laboratory, Sensors and Electrochemical Devices Group, Los Alamos, NM 87545*
[2]*Department of Physics and Astronomy and BioMaPS Institute for Quantitative Biology, Rutgers University, Piscataway, NJ 08854*
[3]*Washington State University Vancouver, Electrical Engineering, Vancouver, WA 98686*

Mixed potential electrochemical sensors continue to be at the forefront of research and development into new sensors for automotive and diesel applications. Much of the interest in these devices naturally arises from the fact that they are zirconia-based sensors derived from the hugely successful automotive lambda sensor, which is a desirable starting point from a durability and cost point of view. The goal of a low-cost, sensitive, and robust NO_x sensor is to improve fuel economy in lean burn gasoline engines; and, a NO_x sensor, when combined with an ammonia sensor with similar attributes, can offer the potential for higher performance after-treatment systems that would lower emissions and improve fuel economy in diesel vehicles.[1] Mixed-potential sensors are electrochemical devices that measure the non-Nernstian potential of a mixture of gases, where the mixed-potential is fixed by the rates of different electrochemical reactions occurring simultaneously at an electrode/electrolyte interface. Employing electrode materials that possess varying catalytic activities towards the redox half reactions has been shown as a successful approach to affect the selectivity mixed-potential response. Moreover, it has been shown that the application of a small bias current to mixed potential sensors that have been designed such that interfacial resistance dominates the overall sensor impedance may offer additional flexibility to control gas selectivity.[2-4]

LANL has developed mixed potential sensors based on the placement of preformed dense electrode materials (Pt or Au wire, oxides such as $La_{1-x}Sr_xCrO_3$; x = 0 to 0.3) within tape cast layers of YSZ.[5] The devices are fired at temperatures sufficient to create mechanical stability while preventing full densification of the electrolyte. Sensors based on Pt and Au wire electrodes have been shown to exhibit preferential response to ammonia (Figure 1a) but unlike what we have shown in previous work with sensors based on chromite electrodes, even with judicious selection of operating temperature, one cannot apply a current bias to completely eliminate a response to the interference gas (contrast elimination of NO_2 response in Figure 1b using -3µA bias with the inability to remove C_3H_6 response across a range of bias currents in Figure 2).[3] In research largely unrelated to electrochemical automotive sensors, the decoding of complex chemical mixtures with a limited number of sensors, or sensor arrays, is of great interest. The mammalian olfactory system is an example of a combinatorial sensor array capable of detecting a large number of analytes using a relatively small number of receptors. The idea of combinatorial recognition has been adapted to artificial arrays in which multiple sensors with partially overlapping selectivities respond to a given analyte.

In this work, we investigate whether the bias-sensitive behavior of mixed potential devices seen in Figure 2 can be analyzed with a modified version of RANSA (Receptor Array Nested Sampling Algorithm), a Bayesian interference tool originally developed for chemical mixture decomposition in biological systems characterized by non-linear response to receptor-ligand

binding.[6] The ability to influence selectivity with different applied bias currents (i.e. the ability to change the magnitude of hydrocarbon response relative to the ammonia response in this type of sensor) in conjunction with Bayesian analysis of the output signal provides a method for measuring target gas species concentration in the presence of interference gases that are known to produce an interfering sensor response. For practical application, two modes of operation may be envisioned: 1) a single mixed potential sensor is utilized and is operated at multiple, discrete bias current points or, 2) multiple mixed potential sensors are utilized operating at specific and fixed bias points, effectively creating a sensor array.
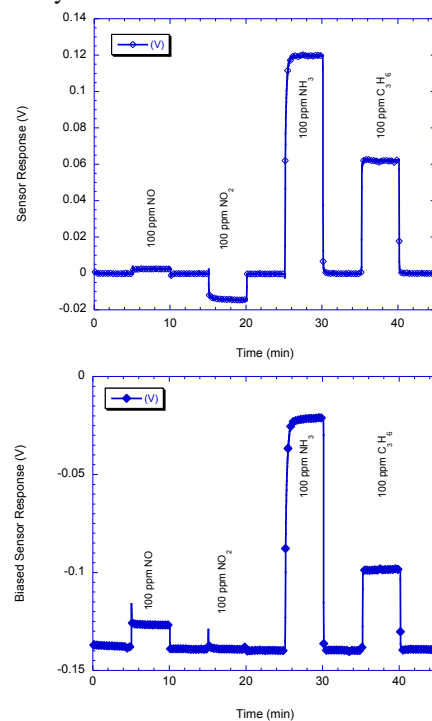

Figure 1: Response of an Au/YSZ/Pt mixed potential sensor to 100 ppm of NO, NO_2, NH_3, and C_3H_6 at 575°C in 10% O_2/balance N_2 at (a) open circuit and (b) -3µA current bias.
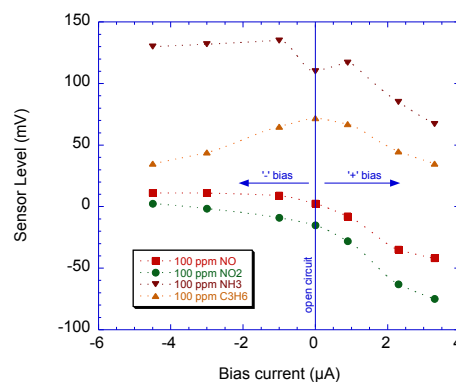

Figure 2: Response of an Au/YSZ/Pt mixed potential sensor to 100 ppm levels of NO, NO_2, NH_3, and C_3H_6 at 575°C in 10% O_2/balance N_2 at various levels of current bias.

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