

Study of YSZ Electrolyte Inks for Preparation of Screen-Printed Mixed-Potential Sensors for Selective Detection of NO_x and NH₃[†]

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† Presented at the Eurosensors 2017 Conference, Paris, France, 3–6 September 2017.

Published: 16 August 2017

Abstract: Among all NO_x reduction approaches, selective catalyst reduction (SCR) system is one the most reliable ways to control NO_x emissions from diesel engine vehicles and trucks. In order to optimize the conversion rates of NO_x and to prevent inducing excessive NH₃ to the air, an NH₃ and NO_x sensor is required. In this study, three different types of YSZ ink have been examined to identify the most effective electrolyte for NO_x and NH₃ sensing. The results have shown that a home-made ink with YSZ powder shows the best sensitivity towards ammonia without polarization and the highest NO₂/NO signal ratio with polarization current of 25 nA.

Keywords: mixed-potential sensor; NO_x; Yttria stabilized Zirconia; NH₃; electrolyte

1. Introduction

Nowadays, one of the biggest concerns of public and politicians, is air pollution with a major focus on poor air quality and its effects on the life in urban areas [1]. In order to decrease this concern, a lot of NO_x (which mostly contribute to NO₂ concentrations) reduction approaches have been developed recently which among them Selective Catalytic Reduction system (SCR) is one of the most cost-effective and fuel-efficient diesel engine NO_x emissions control technologies. Since the DeNO_x selective catalytic reduction system uses ammonia as the reducing agent, the concern of NH₃ being injected into the atmosphere has been rose up in heavy duty diesel vehicles [2]. J.P. Viricelle et al. in 2015 [3] have developed mixed-potential selective NO₂ sensors. Based on this study, we aim to develop sensors for selective detection of both NO_x and NH₃ for automotive exhaust.

2. Materials and Methods

In this study, different sensors are fabricated by using commercial and home-made ink by the method of screen-printing. The used inks are consisting of a powder of inorganic material (active element), a binder and an organic solvent. As solid electrolyte we used a commercial YSZ ink (named ink A) sintered at 1380 °C or 1480 °C and also home-made ink using YSZ powder (named ink B) sintered at 1380 °C. For the electrodes, we used gold (ESL 8880-H) and platinum (ESL 5545) commercial inks and for the connectors we used the same ink as gold electrode. The welding areas were made from a palladium and silver commercial ink (ESL 9635BT). A schematic figure of fabricated sensors is shown in Figure 1a.

In order to evaluate the performance of the fabricated planar sensors, the response to different pollutant gases such as CO, NH₃, NO₂ and NO in respective amounts of 100, 20, 100 and 100 ppm are studied at 450 °C and in a base gas composed of 12% O₂ and 1.5% H₂O, balanced with N₂. The test bench that we use in this study is presented in Figure 1b. The gases are controlled by mass flow

regulators and arrive first in a mixing chamber before being sent to two cells which each contains one sensor. A vaporizer allows performing the tests in humid atmosphere.

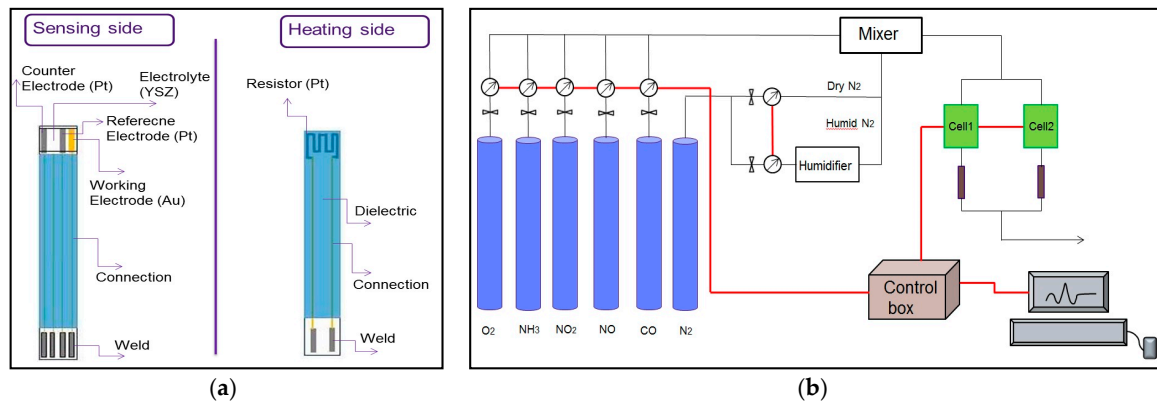


Figure 1. A schematic figure of: (a) solid-state fabricated gas sensors; (b) experimental set-up at EMSE.

In addition, by applying a constant polarization current of 25 nA between working electrode (Au) and counter electrode (Pt), the sensor responses (ΔV) are measured between working electrode and reference electrode (Pt) according to Equation (1).

$$\Delta V = V_{RE}(Pt) - V_{WE}(Au), \quad (1)$$

V_{RE} : Potential of the reference electrode; V_{WE} : Potential of the working electrode.

3. Results and Discussion

In order to take into account irreproducibility of the sensors due to fabrication process, all tests are repeated with two sensors (1 and 2). The OCV values (Open Circuit Voltage, no polarization) were measured in the base gas for 30 min upon $i_{pol} = 0$. In Figure 2, we observe the expected response in the opposite direction for reducing gas such as CO, NH₃ and NO (positive comparing with the baseline) and the oxidizing gas NO₂ (negative to baseline).

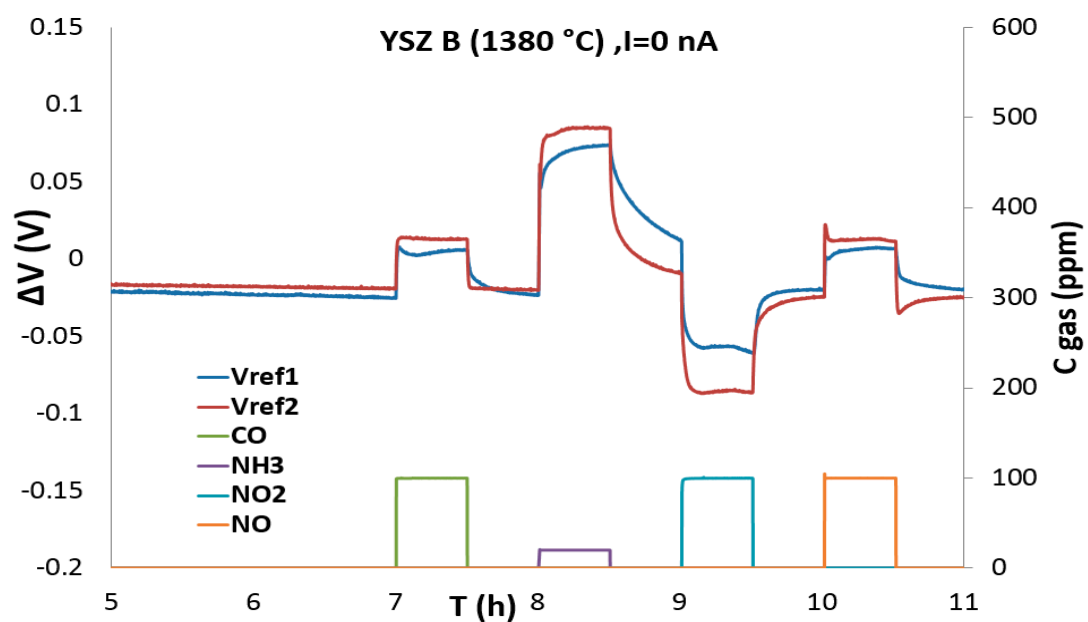


Figure 2. Responses (ΔV) of the three-electrodes sensors with YSZ B at 450 °C during pulses of CO (100 ppm), NH₃ (20 ppm), NO₂ (100 ppm) and NO (100 ppm) in base gas without polarization current.

Since NO_2 is an oxidizing gas, the galvanostatic mode can only produce the electro-chemical reduction of NO_2 at working electrode. Figure 3 shows the variations of the potential (ΔV) for sensors with YSZ B at 450 °C for different gases by applying a polarization current of 25 nA. In these conditions it can be obviously seen that the responses to other interfering gases such as CO and NH_3 are almost removed while there is relatively a good selectivity towards NO_2 .

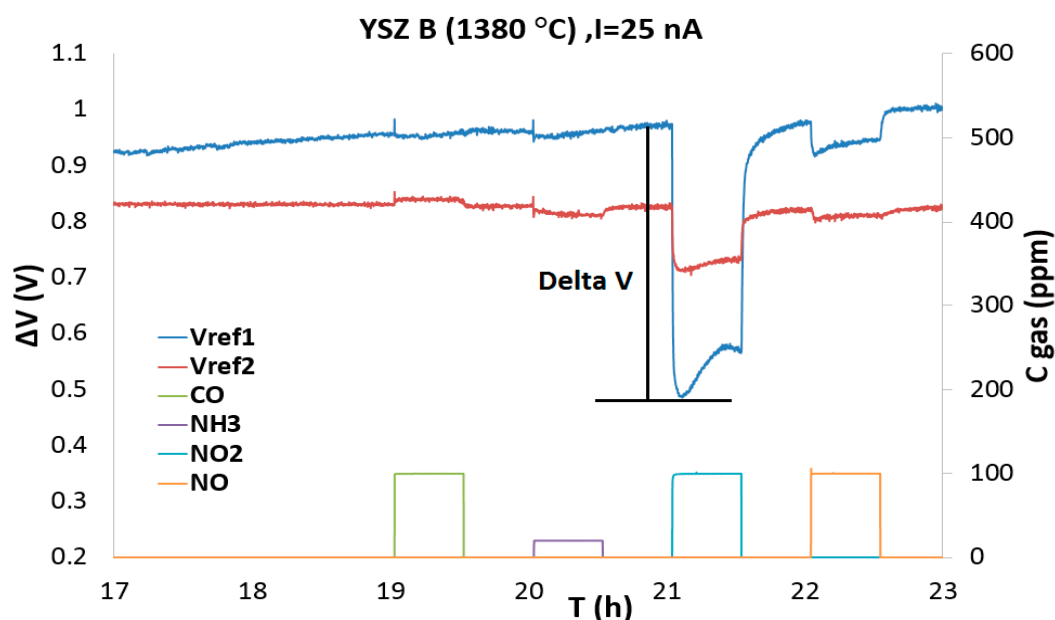


Figure 3. Responses (ΔV) of the three-electrodes sensors with YSZ B at 450 °C during pulses of CO (100 ppm), NH_3 (20 ppm), NO_2 (100 ppm) and NO (100 ppm) in base gas with a polarization current of 25 nA.

The responses of different sensors (YSZ A 1380 and 1480 °C, YSZ B 1380 °C) to 20 ppm of ammonia are shown in Figure 4. This bar chart clearly illustrates that without polarization the sensors with YSZ B give the most significant responses toward NH_3 . Regarding NO_2/NO signal ratio, although the sensors based on commercial YSZ ink A sintered at 1380 °C show the highest response to both gases, Figure 5 shows that the most relevant sensor in regards of NO_2 response is the one with YSZ B.

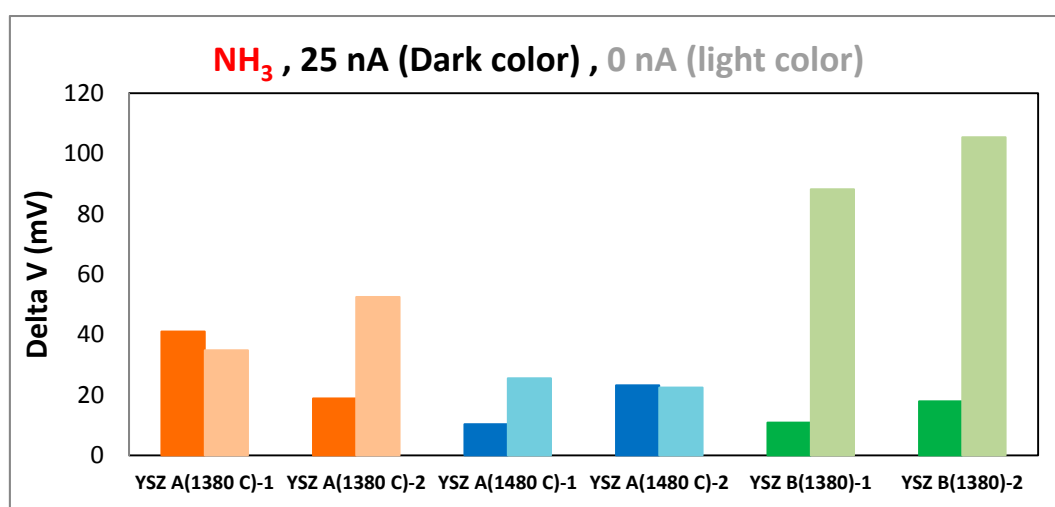


Figure 4. The responses of different sensors to 20 ppm of ammonia at 450 °C.

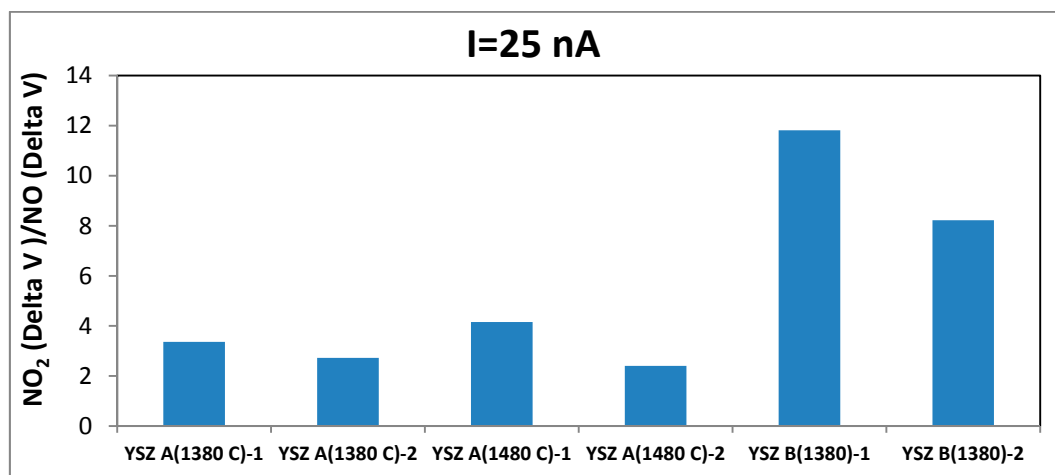


Figure 5. NO₂/NO signal ratio of different sensors at 450 °C (100ppm for each gas).

4. Conclusions

Comparing all these results, it can be concluded that sensors made with home-made ink B give more confident results regarding NO_x and ammonia gases. Further investigations on chemical composition of these YSZ inks and structure of resulting electrolyte film will be performed in order to explain such different sensor responses.

Conflicts of Interest: The authors declare no conflict of interest.

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