

Development of an Integrated in-Vehicle Driver Breath Ethanol System Based on α -Fe₂O₃ Sensing Material [†]

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Abstract:

Alcohol abuse is the dominant cause of fatal car accidents (about 25% of all road deaths in Europe). The large-scale implementation of systems aimed at the realization of in-vehicle driver breath ethanol detection is therefore highly demanding. For this reason, we devoted our attention to the design of an inexpensive and reliable breath alcohol sensor for use in an Advanced Driver Assistance System (ADAS). The main challenge in the development of this sensor is related to the complexity of breath composition and its high humidity content, coupled with the high dilution of breath reaching the sensor. In this work, a simple α -Fe₂O₃ film-based sensor has been developed and validated in laboratory tests. Tests were also performed by placing the ethanol sensor within the casing of a car upper steering column, for simulating real driving conditions. Using an array provided with the developed ethanol sensor and humidity, temperature and CO₂ sensor it was possible to differentiate the signal of a driver's breath before and after alcohol consumption.

Keywords: gas-sensing; ethanol; iron oxide; sensing materials; ADAS

1. Introduction

Advanced Driver Assistance Systems (ADAS) are intelligent systems that assist the driver in a variety of ways [1]. They may be used to provide useful traffic information but may also be used to evaluate whether or not the driver is in physical conditions to drive. Among other driver-related risk factors (e.g. drug intake or altered emotional state), alcohol abuse remains the dominant cause of fatal car accidents (about 25% of all road deaths in Europe). Based on these concerns, we started a research activity with the main objective to develop an in-vehicle driver breath ethanol detection system [2].

To facilitate the large-scale implementation of these systems, the design of inexpensive, reliable and easy to fabricate sensors is required. Conductometric sensors apply very well for this scope, possessing all the required characteristics [3]. Many examples of ethanol sensors have been developed so far, showing a remarkable sensing capacity [4–6]. In particular, we have shown that α -Fe₂O₃ is an ideal candidate as a sensing material to be used in breath ethanol conductometric sensors [7,8].

Based on the previous work, here the α -Fe₂O₃ material has been employed for fabricating conductometric gas sensors to be used for breath ethanol detection in ADAS systems. Preliminary laboratory tests were performed to validate the fabricated sensors and optimize the operating conditions. Then, tests were performed by placing the ethanol sensor within the casing of a car upper steering column, for simulating driving position. The main challenge in the development of this system is related to the complexity of breath composition and its high humidity content, coupled with the high dilution of breath reaching the sensor. For this reason, it was necessary to install the ethanol sensor into an

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array that also contains humidity, temperature and CO₂ sensors (the latter breath component employed as an internal standard). Through the simultaneous use of these three sensors, it was demonstrated possible to differentiate the signal of a driver's breath before and after alcohol beverage consumption.

2. Materials and Methods

2.1. Material Preparation

For the synthesis of α -Fe₂O₃ material, a simple Pechini sol-gel process was employed [6,7]. This method is based on the polymerization of metallic citrate by ethylene glycol. Iron nitrate (Fe(NO₃)₃ · 9H₂O), citric acid (C₆H₈O₇ · H₂O), poly(vinylpyrrolidone) and ethylene glycol (C₂H₆O₂) were purchased from Merck. All the chemicals were used as received and without further purification. Double distilled water was used to prepare precursor solutions.

First, the appropriate amount of Fe(NO₃)₃ · 9H₂O was dissolved in distilled water at 70 °C for 1h under magnetic stirring to make a 0.5 M Fe³⁺ solution. Then this solution was mixed with PVP solution with a molar ratio of [PVP]/[Fe³⁺] = 1. On the other hand, citric acid was dissolved in distilled water at 70 °C for 30 min. Afterwards, the citric acid solution was added slowly to the Fe³⁺/PVP solution with stirring. Citric acid to Fe³⁺ molar ratio was 2. Then the esterification agent, i.e. ethylene glycol (EG), was added with a molar ratio [Citric acid]/[EG] = 2 while stirring and heating the solution. The final solution was reflux at 100 °C for 2h. The clear yellow-coloured precursor solution obtained was dried at 120 °C for 12h to obtain the precursor powders. Finally, the amorphous powders were calcined at 550 °C in air for 3h using a muffle furnace, to obtain iron oxide nanoparticles.

2.2. Sensor Preparation and Sensing Tests

Sensor devices were fabricated by spray coating method as follows. An appropriate volume of the α -Fe₂O₃ suspension was sprayed on alumina substrates (3×6 mm) supplied with interdigitated Pt electrodes and a heating element on the backside. The sensors prepared were let drying at room temperature then heat-treated at 400 °C to obtain a mechanically stable sensing layer.

Measurements were performed both under a dry and wet (50% relative humidity) air total stream of 100 mL/min, collecting the sensors resistance data in the four-points mode using an Agilent 34970A multimeter. Electrical measurements were carried out at the working temperature 300 °C. Sensing tests were performed in a lab apparatus that allows to operate at controlled temperature and to perform resistance measurements while varying the ethanol concentration from 12.5 to 400 ppm.

The gas response was defined as the ratio $R_{\text{air}}/R_{\text{gas}}$, where R_{air} represents the electrical resistance of the sensor in dry air and R_{gas} is the electrical resistance of the sensor at different ethanol concentration. Response time, t_{res} , was defined as the time required for the sensor resistance to reach 90% of the equilibrium value after ethanol is injected and recovery time, t_{rec} , was taken as the time necessary for the sensor resistance to reach 90% of the baseline value in air.

3. Results

3.1. Laboratory Sensing Tests

The characteristics of the developed α -Fe₂O₃ sensor were first evaluated in laboratory tests. Based on the preliminary results, the temperature of 300 °C was selected as the operating temperature. Figure 1a shows the sensor behaviour versus ethanol concentration ranging from 400 to 12.5 ppm, at this temperature. A decrease in the resistance was noticed with the concentration of ethanol. The sensor shows a well reversible response (see Figure 1b) with a fast response and recovery (about 10 sec. and 60 sec, respectively).

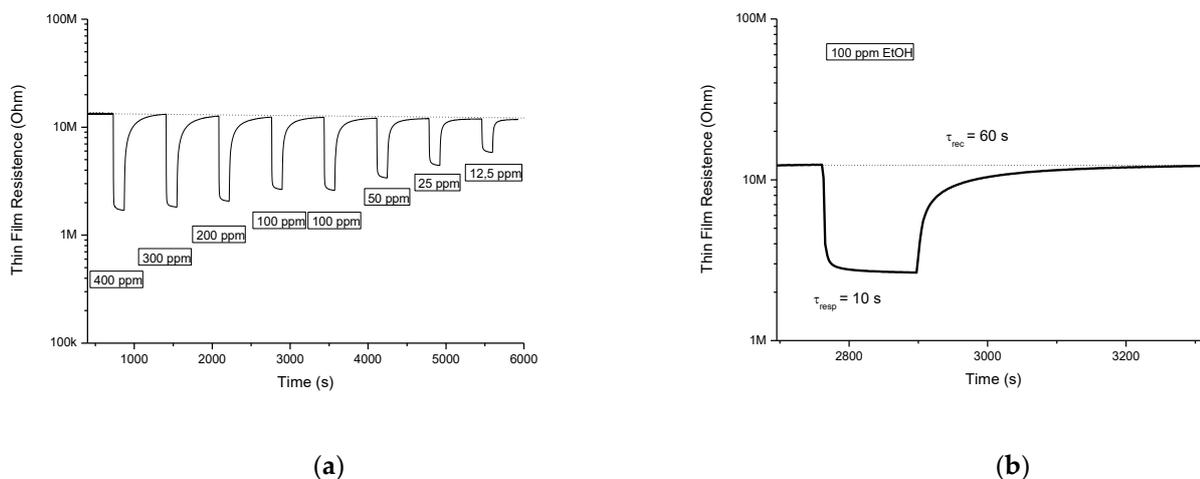


Figure 1. a) Response of the sensor to a variable concentration of ethanol in dry air at 300°C; b) Response of the sensor to an ethanol pulse of 100 ppm. The measured response and recovery times are reported.

From the above test, the calibration curve shown in Figure 3 has been obtained. Plotting the data in a log-log graph, a well linear correlation between the sensor resistance and the ethanol concentration is observed. In the same graph is also plotted the calibration curve for the same sensor obtained in conditions of higher relative humidity (50 % RH). Breath is highly saturated with water vapour, therefore the sensor performances mustn't be influenced by changing the humidity level. Interestingly, the sensor signal we collected in different humidity conditions appears to be independent from this variable.

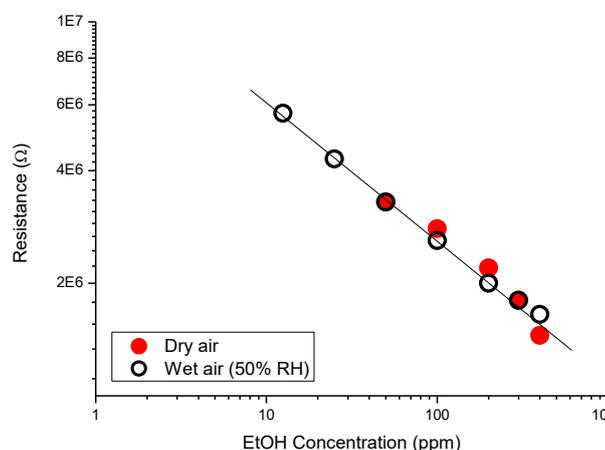


Figure 2. Calibration curve at 300°C for the $\alpha\text{-Fe}_2\text{O}_3$ sensor in *dry* and *wet* condition.

3.4. Ethanol Sensor Implementation in ADAS Systems

Then, the research work continued with the installation of the ethanol sensor inside the casing of a car upper steering column, for simulating real driving conditions (see Figure 3). Humidity, temperature and CO_2 sensors were also installed. CO_2 concentration detected was used to take account for the dilution of the breath sample. A suitable chamber was therefore designed and built to contain the sensor array.



Figure 3. Pictures showing the location of the ethanol sensor inside the casing of a car upper steering column (left) and the driver position during the test, simulating the real driving conditions (right).

After having installed the sensors some preliminary tests to validate their correct functioning were carried out, especially to verify if the breath of the driver may be detected well by the sensor array located at a distance of 30-50 cm from the driver's mouth. Indeed, in the condition adopted, breath is diluted with ambient air by a factor of as much as 5-10 [8].

The graphs reported in Figure 4 show the signals coming from the ethanol, humidity, temperature and CO₂ sensors, recorded when the driver was in different conditions, i.e.: before drinking alcoholic beverages, therefore in the absence of alcohol in the breath (white zone, left column), and subsequently after drinking an alcoholic beverage (red zone, right column), and then in the presence of alcohol in the breath.

By analyzing and comparing these graphs, we can see how after drinking the alcoholic beverage, the signal of the ethanol sensor undergo a quick decrease, clearly noticeable in the ethanol sensor trace. With time the signal of the ethanol sensor tends to decrease, as expected by considering the well dynamic process of ethanol absorption, metabolism, and elimination from the body after its ingestion [9].

The measurements carried out demonstrate that the sensor module designed and built, correctly fulfils its functions, thus being able to monitor the level of ethanol in the driver's breath in real-time.

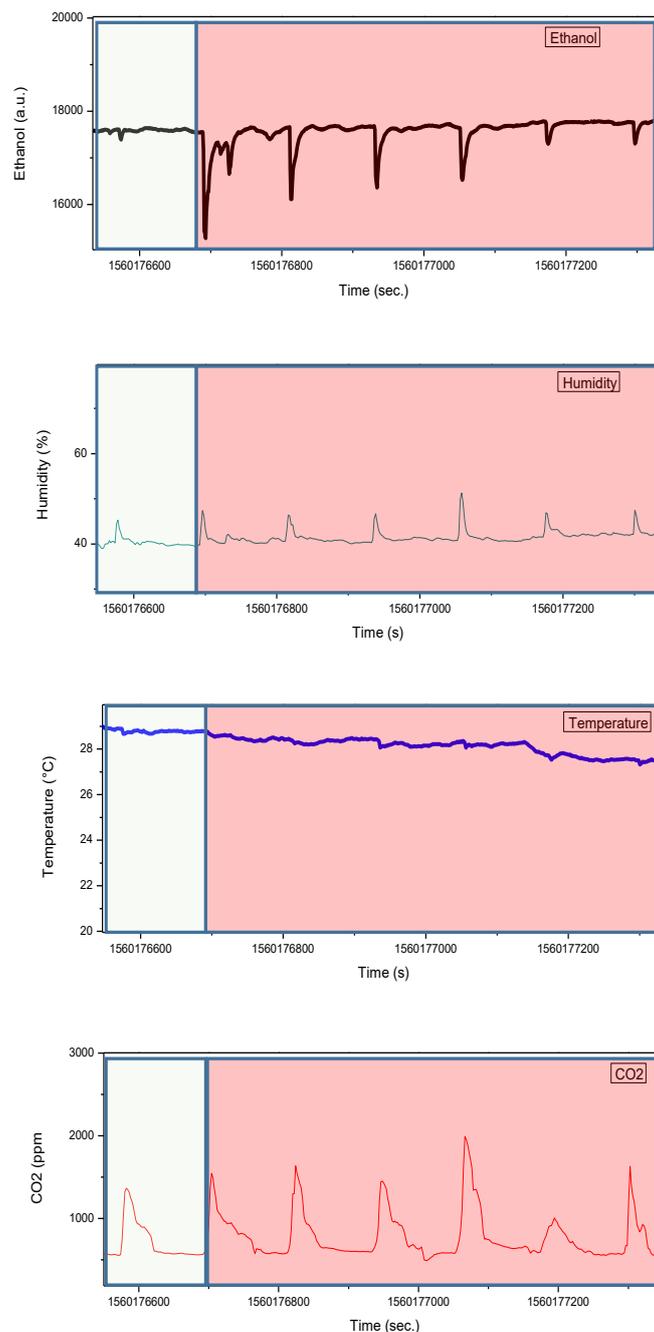


Figure 3. Signals from the ethanol, humidity, temperature and CO₂ sensors, recorded before drinking alcoholic beverages (white zone, left column), and subsequently after drinking an alcoholic beverage (red zone, right column).

4. Conclusions

An in-vehicle driver breath ethanol detection system has been realized by using a simple α -Fe₂O₃ film-based conductometric sensor for detecting breath ethanol. Using an array provided with the developed ethanol sensor and humidity, temperature and CO₂ sensor, it was possible to differentiate the signal of a driver's breath before and after alcohol consumption, thus demonstrating that the sensor module developed, can monitor the level of ethanol in the driver's breath in real-time.

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