Development of an Integrated In-Vehicle Driver Breath Ethanol System Based on $\alpha$-Fe$_2$O$_3$ 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 in high demand. 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 $\alpha$-Fe$_2$O$_3$ film-based sensor was developed and validated in laboratory tests. Tests were also performed by placing the ethanol sensor within the casing of the upper steering column of a car to simulate real driving conditions. Using an array provided with the developed ethanol sensor and humidity, temperature and CO$_2$ sensors, 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 (ADASs) 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 condition 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). It is well known that too much alcohol in the blood leads to various serious effects on human health and the condition of drivers [2,3]. Alcohol interferes with the brain, affecting the way that it looks and works and reducing movement coordination. Further, alcohol can slow reflexes, slow eye muscle function, and alter visual perception. These conditions are very critical for car drivers, so maintaining an acceptable blood alcohol level is necessary in order to limit car accident risks.

Based on these concerns, we initiated research activity with the main objective of developing an in-vehicle driver breath ethanol detection system [4]. To facilitate the large-scale implementation of these systems, the design of inexpensive, reliable and easily fabricated sensors is required. Conductometric sensors apply very well to this scope, as they possess all of the required characteristics [5]. Many examples of ethanol sensors have been developed and show a remarkable sensing capacity [6–8]. In particular, we have shown that $\alpha$-Fe$_2$O$_3$ is an ideal candidate as a sensing material to be used in breath ethanol conductometric sensors [9,10].

Based on previous work, in this research, the $\alpha$-Fe$_2$O$_3$ material was employed for fabricating conductometric gas sensors to be used for breath ethanol detection in ADASs. 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 the upper steering column of a car to simulate the 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 in an array that also contains humidity, temperature and CO$_2$ sensors (the latter breath component is employed as an internal standard). Through the simultaneous use of these three sensors, it was 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-Fe$_2$O$_3$ 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(NO$_3$)$_3$·9H$_2$O), citric acid (C$_6$H$_8$O$_7$·H$_2$O), poly(vinylpyrrolidone) and ethylene glycol (C$_2$H$_4$O$_2$) were purchased from Merck. All of 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(NO$_3$)$_3$·9H$_2$O was dissolved in distilled water at 70 °C for 1 h under magnetic stirring to produce a 0.5 M Fe$^{3+}$ solution. Then, this solution was mixed with PVP solution with a molar ratio of [PVP]/[Fe$^{3+}$] = 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 Fe$^{3+}$/PVP solution with stirring. The citric acid to Fe$^{3+}$ molar ratio was 2. Then the esterification agent, i.e., ethylene glycol (EG), was added with a molar ratio of [citric acid]/[EG] = 2 while stirring and heating the solution. The final solution was refluxed at 100 °C for 2h. The clear yellow-colored precursor solution obtained was dried at 120 °C for 12 h to obtain the precursor powders. Finally, the amorphous powders were calcined at 550 °C in air for 3 h using a muffle furnace to obtain iron oxide nanoparticles.

2.2. Sensor Preparation and Sensing Tests

Sensor devices were fabricated by the spray-coating method as follows. An appropriate volume of the α-Fe$_2$O$_3$ suspension was sprayed on alumina substrates (3 × 6 mm) supplied with interdigitated Pt electrodes and a heating element on the backside. The prepared sensors were dried at room temperature and then heat-treated at 400 °C to obtain a mechanically stable sensing layer. The structure of the fabricated ethanol sensor is shown in Figure 1.

![Sensor](image)

**Figure 1.** Photo of the fabricated ethanol sensor.
Measurements were performed under both a dry and wet (50% relative humidity) air stream of 100 mL/min in total, and the sensor resistance data were collected in four-point mode using an Agilent 34970A multimeter. Electrical measurements were carried out at a working temperature of 300 °C. Laboratory sensing tests were performed in a lab apparatus that allows operation at controlled temperature and the performance of 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 $R_{\text{air}}$ represents the electrical resistance of the sensor in dry air, and $R_{\text{gas}}$ is the electrical resistance of the sensor at different ethanol concentrations. Response time, $t_{\text{res}}$, was defined as the time required for the sensor resistance to reach 90% of the equilibrium value after ethanol is injected, and recovery time, $t_{\text{rec}}$, 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 $\alpha$-Fe$_2$O$_3$ sensor were first evaluated in laboratory tests. Based on the preliminary results, a temperature of 300 °C was selected as the operating temperature. Figure 2a shows the sensor behavior versus ethanol concentration, which ranged from 400 to 12.5 ppm at this temperature. A reversible variation in the resistance was observed with the concentration of ethanol. As usually verified for metal oxide-based conductometric sensors, response and recovery times are dependent on the alcohol concentration. This is also the case for our sensor. Response (8–15 s) and recovery (120–45 s) times were observed for ethanol concentrations ranging from 400 to 12.5 ppm. At the intermediate concentration of 100 ppm, the sensor showed a noticeable reversible response (see Figure 2b) with a fast response and recovery (about 10 s and 60 s, respectively).

![Figure 2a](image1.png) ![Figure 2b](image2.png)

**Figure 2.** (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 was obtained. Plotting the data in a log–log graph, a high linear correlation between the sensor resistance and the ethanol concentration is observed. The same graph also shows the calibration curve for the same sensor obtained in conditions of higher relative humidity (50% RH). Breath is highly saturated with water vapor; therefore, the sensor performance must not be influenced by changes in the humidity level [11–13]. Interestingly, the sensor signal that we collected in different humidity conditions appears to be independent of this variable.
15 min, for a total weight of 17.5 g of ingested alcohol (0.25 g of alcohol per kilogram of body).

3.2. Ethanol Sensor Implementation in ADASs

Then, the research work continued with the installation of the ethanol sensor in the casing of the upper steering column of a car to simulate real driving conditions (see Figure 4). A diagram of the designed and constructed module consisting of the ethanol sensor used in this research was reported in a previous paper [14]. Humidity, temperature and CO₂ sensors were also installed. The detected CO₂ concentration was used to account for the dilution of the breath sample. A suitable chamber was therefore designed and built to contain the sensor array.

![Figure 3. Calibration curve at 300 °C for the α-Fe₂O₃ sensor in dry and wet conditions.](image)

**Figure 3.** Calibration curve at 300 °C for the α-Fe₂O₃ sensor in dry and wet conditions.

After installing the sensors, some preliminary tests to validate their correct functioning were carried out, especially to verify if the breath of the driver can be well detected by the sensor array when it is located at a distance of 30–50 cm from the driver’s mouth. Indeed, in the conditions adopted, breath is diluted with ambient air by a factor as high as 5–10 [15,16].

One subject (male, 70 kg) was used for the test. He was allowed to drink two glasses (50 mL in total) of a commercial alcoholic beverage (44% of ethanol in v/v) in less than 15 min, for a total weight of 17.5 g of ingested alcohol (0.25 g of alcohol per kilogram of body mass). Measurements were performed before drinking and repeated every 30 min until the breath alcohol level returned to the background level (approximately 3 h).

The graphs reported in Figure 5 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 and therefore in the absence of alcohol in the breath (white zone, left column) and subsequently after drinking an alcoholic beverage and thus in the presence of alcohol in the breath (red zone, right column).

Figure 5. Signals from the ethanol, humidity, temperature and CO$_2$ sensors, recorded before drinking alcoholic beverages (white zone, left column) and subsequently after drinking an alcoholic beverage (red zone, right column).

By analyzing data coming from the ethanol sensor, we can see that after the alcoholic beverage is consumed, the signal of the sensor undergoes a quick increase, reaching a maximum after about 30 min (see Figure 6). Subsequently, the signal of the ethanol sensor tends to decrease, as expected by considering the well-known dynamic process of ethanol absorption, metabolism and elimination from the body after its ingestion [17].
Figure 6. Response from the ethanol sensor during the entire duration of breath test.

The measurements carried out demonstrate that the designed and built sensor module correctly fulfills its functions and is thus able to monitor the level of ethanol in the driver’s breath in real time.

4. Conclusions

An in-vehicle driver breath ethanol detection system was 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 sensors, it was possible to differentiate the signal of a driver’s breath before and after alcohol consumption, thus demonstrating that the developed sensor module can monitor the level of ethanol in the driver’s breath in real time.

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