Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

The use of an e-tongue for discriminating ethanol/water mixtures and determination of their water content

Dalton P. de Queiroz [a,e], Ariovaldo de Oliveira Florentino [b,1], Juliana Catarina Bruno [b],
José H. Dias da Silva [c], Antonio Riul Jr. [d,e], José A. Giacometti [e,f,*]

[a] Universidade Estadual de Mato Grosso do Sul, UEMS, 79804-970, Dourados, MS, Brazil
[b] Instituto de Biociências, UNESP, 18.618-000 Botucatu, SP, Brazil
[c] Faculdade de Ciências, UNESP, 17.033-360, Bauru, SP, Brazil
[d] Instituto de Física Gleb Wataghin,UNICAMP, 13083-859, Campinas, SP, Brazil
[e] Faculdade de Ciências e Tecnologia, UNESP, 19060-900 Presidente Prudente, SP, Brazil
[f] Instituto de Física de São Carlos, USP, 13566-590 São Carlos, SP, Brazil

ARTICLE INFO

ABSTRACT

This paper discusses the applicability of an electronic tongue (e-tongue) based on capacitance measurements to determine the water content in ethanol. The e-tongue consisted of an array of interdigitated electrodes coated with ultrathin films of gallium nitrate and titanium dioxide, which were robust against attack by ethanol. Principal Component Analysis (PCA) was used to treat the capacitance data for discriminating ethanol/water mixtures even in cases with very small water contents. Discrimination is easier if the water added to ethanol contains ions, as is the case of tap water or if NaCl is added to the mixtures. With this e-tongue we were able to quantify the water content through a linear relationship between the first principal component (PC1) and the added water to the biofuel. Therefore, we have proven to be possible to measure the water content precisely, which is one of the major problems in ethanol biofuel adulteration nowadays.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

According to IUPAC definition an electronic tongue (e-tongue) is a multisensory system composed of low-selective sensors, using advanced mathematical techniques for signal processing based on pattern recognition and multivariate analysis [1]. These systems appeared as a suitable tool to distinguish between different complex liquid systems, as in the analysis of wine, beer, coffee, pollutants in water, food, juices, milk and mineral water [2–8]. Some advantages in comparison to conventional analytical methods include a fast, efficient and cheaper analysis, and easy interpretation of the results with no need of trained personnel. This has generated strong interest in the industry requiring quality control of foodstuff. The most used techniques in e-tongue systems are potentiometry [9–12], cyclic voltammetry [13–16], impedance spectroscopy [17–21]. They are all based on the global selectivity of sensing units immersed in a liquid sample.

Ethanol has been an alternative biofuel produced from renewable resources with an increasing global claim as the crop carbon sequestration substantially balances the amount of carbon emitted into the atmosphere. Brazil is a leading country in the use of ethanol biofuel in flex vehicles that are able to run using ethanol, gasoline and their mixtures. In addition, anhydrous ethanol is added into gasoline in Brazil to increase the octane rating. The amount of water in the ethanol biofuel is regulated by Brazilian legislation [22]; the anhydrous ethanol fuel (AEF) must not contain more than 0.4% vol. of water, while 6.5% vol. of water is the maximum allowed for hydrous ethanol fuel (HEF). The quality control of ethanol is an important issue since the most common procedure for adulteration is addition of non-pure water above required standards, resulting in an off-specification product that can damage or produce malfunction in car engines.

Several techniques are used to measure [23] the amount of water in the ethanol biofuel, but low-cost techniques are still necessary. Bueno and Paixão [24] proposed a copper interdigitated bare electrode, which was able to determine the water content through electrical capacitance measurements at distinct frequencies. Ultrasonication was also proposed to measure water content in ethanol biofuel [25].

Here, we address the use of an e-tongue system to determine the water content in ethanol/water mixtures, with the challenge to build sensing units resistant to the ethanol chemical attack. A comparison was made with addition of ultrapure, tap water and sodium chloride salt solution in ethanol, and the results were processed using Principal Component Analysis (PCA). We also address the possibility to measure the water content in ethanol biofuel.

2. Experimental

Gold interdigitated electrodes (IDE) were deposited on glass slides consisting of 50 pairs of digits 5 mm long, 10 μm width, separated 10 μm from each other. Four sensing units were used: one bare IDE and three electrodes coated with thin films of gallium nitrate (GaN), titanium oxide (TiO_2) and titanium oxide doped with 1 mass % of silver (TiO_2–Ag). Titanium oxide and titanium oxide doped with 1 mass % of silver were deposited by the sol–gel method [26]. Titanium isopropoxide (Agros Organics) was used as starting material and isopropyl alcohol (Mallinckrodt) as solvent. Acetic acid (J.T. Baker) and a solution of nitric acid (Merck) were added to promote the hydrolysis polycondensation reaction, where the acetic acid acted as the chelant agent in the molar rate of 1:4 (vol.) of the isopropoxide nitric acid. This sol (viscosity of 20 cP) was spin coated on top of the IDEs using a rotation speed of 1000 rpm, after which the electrodes were further heated and kept at 250 °C for 12 h, producing 200 nm thick films with roughness ranging from 1.7 to 3.5 nm in 10 μm^2, determined by AFM analysis using a Nanosurf Easy Scan AFM apparatus. Gallium nitrate was sputtered onto the IDEs in a RF-magnetron sputtering setup especially assembled to grow III–V compound semiconductor films, resulting in ~60 nm films [27]. A metallic Ga target (7N-purity) and different N2/H2/Ar gas flow ratios (6N-purity) were used in the sputtering process. The films were uniform according to optical microscopy (100×) images (results not shown).

Impedance spectroscopy measurements with the sensing units were performed using an impedance analyzer (Solartron 1260A) in the range between 1 Hz and 1 MHz, with 50 mV of applied sinusoidal voltage. Results are given in terms of the real part of the electrical capacitance as a function of frequency. Briefly, at lower frequencies (<100 Hz) the electrical response is governed by double-layer effects, while at intermediate frequencies (kHz region) it is governed by the film coating the IDEs and at higher frequencies (>100 kHz) by geometric capacitance effects [28,29].

For the e-tongue measurements, we used a computer controlled setup [30] that allows for simultaneous use of up to eight sensing units. Responses were analyzed at 1 kHz, because capacitance measurements at this frequency are sensitive to changes in the film properties due to the liquid sample [28]. The results were analyzed with the non-supervised method of Principal Component Analysis [30] as it is largely employed in this sort of application [21]. The experimental setup performs automatically the PCA analysis, displaying it on the computer screen as a PCA plot [31]. Impedance measurements were performed immersing all sensing units in a small beaker with ethanol and ethanol/water mixtures. Measurements were taken using 10 mL aliquots from an initial volume of 100 mL. For e-tongue measurements, ten readings of capacitance were performed after immersing the sensing units during 5 min in the liquids, which was sufficient to stabilize readings. After each measurement, the sensing units were washed with ultrapure water acquired from a Millipore Direct Q5 system model and gently dried flushing dry air. Measurements were taken at room temperature (25 ± 0.1 °C), controlled by a thermostatic bath (Marconi MA-184). The same set of sensing units was employed for all measurements described here.
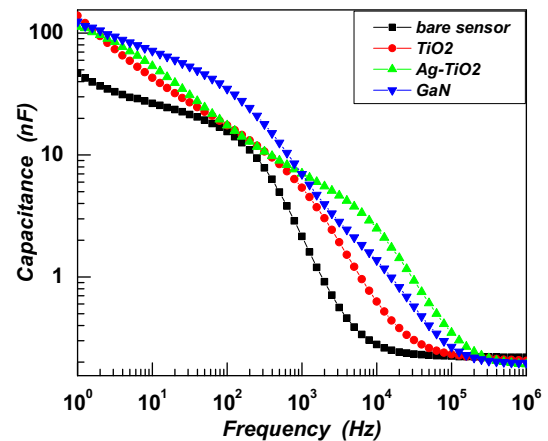

Fig 1. Capacitance response of the sensing units immersed in Milli-Q water.

Anhydrous ethanol (AEF) was obtained directly from the ethanol plant (UNIVALEM, Valparaíso, SP, Brazil), produced from sugar cane and containing 0.4% vol. of water (as measured in a UNIVALEM laboratory), compliant with Brazilian standards. Hydrous ethanol biofuel (HEF) also supplied by UNIVALEM (4.9% vol. of water) was used in some measurements. Anhydrous ethanol was mixed with water (Milli-Q or tap water) in different percentages to prepare the mixtures. Samples of hydrous ethanol sold as car biofuel (for flex propelled ethanol/gasoline vehicles) were acquired in different fuel stations and used for blind test measurements. Tap water was collected in Presidente Prudente (SP, Brazil) (maximum content of 0.2 mg/L of chlorine and 0.7 mg/L of fluorine for human consumption), following Brazilian standards [32].

3. Results and discussion

3.1. The fingerprint of sensing units

Fig. 1 exhibits capacitance curves of the sensing units immersed in Milli-Q water. Results obtained after immersing them for 5 min in the Milli-Q water indicate that the presence of films on interdigitated electrodes alters the response of the bare IDE, creating a fingerprint of the liquid under analysis [29]. The capacitance spectrum varied with the film deposited in practically all frequency regions, probably reflecting the different dielectric constants of the thin films. At very high frequencies (near 1 MHz) there was almost no change in capacitance because the geometry of the IDEs was the same.

Fig. 2 shows measured capacitances with sensing units immersed in anhydrous ethanol. At 1 kHz a 0.3 nF variation is observed, smaller than that in Fig. 1, indicating a lower sensitivity of the system to ethanol. As the sensing units are more sensitive to water than ethanol, we took it as a tool to determine the water content in ethanol/water mixtures.

The electrical response of the TiO_2 thin film at distinct AEF/Milli-Q water concentrations (from 5 to 60% vol. of water added in AEF) is illustrated in Fig. 3, which also includes the result for the ethanol fuel (HEF, 4.9% vol. of water) for comparison. Similar fingerprints were observed (not shown here) for the other sensing units immersed in these AEF/Milli-Q water mixtures. The response at high frequencies (>100 kHz) is due to the capacitive response of ethanol/water mixtures, where capacitance increased with the water content owing to the higher dielectric constant for water (at room temperature $\varepsilon = 80$ for water and 25 for ethanol).