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ScienceDirect
Biosensors and Bioelectronics 22 (2007) 2618–2623
BIOSENSORS & BIOELECTRONICS
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A composite sensor array impedentiometric electronic tongue Part I. Characterization

G. Pioggia [a,*], F. Di Francesco [b], A. Marchetti [a], M. Ferro [a], A. Ahluwalia [a]

[a] *Interdepartmental Research Center "E. Piaggio", Faculty of Engineering, University of Pisa, Italy*
[b] *Department of Chemistry and Industrial Chemistry, University of Pisa, Italy*

Received 15 July 2006; received in revised form 19 September 2006; accepted 25 October 2006
Available online 11 December 2006

Abstract

A study aimed at the characterization of five compounds with different chemical characteristics and gustative perceptions by measuring the variations of the electrical impedance of a composite sensor array is presented. The array was composed of five sensors of three different types based on carbon nanotubes or carbon black dispersed in polymeric matrices and doped polythiophenes. Measurements were carried out by evaluating the electrical impedance of the sensor array at a frequency of 150 Hz, and the data acquisition process was automated; a mechanical arm and a rotating platform controlled by a data acquisition card and a dedicated software allowed the sequential dipping of sensors in the test solutions. Fifty different solutions eliciting the 5 basic tastes (sodium chloride, citric acid, glucose, glutamic acid and sodium dehydrocholate for salty, sour, sweet, umami and bitter, respectively) at 10 concentration levels comprising the human perceptive range were analysed. More than 100 measurements were carried for each sample in a 4-month period to evaluate the system repeatability and robustness. The impedentiometric composite sensor array is shown to be sensitive, selective and stable for use in an electronic tongue.

Keywords: Composite sensor array; Impedentiometric electronic tongue; Carbon nanotubes; Carbon black; Hydrogel; Polythiophenes

1. Introduction

Despite the fact that vision and hearing have always monopolised scientific and lay interests, the chemical senses have been the object of study since ancient times. Probably the first description of anosmia is due to Theophrastus, the Greek philosopher of the Peripatetic school who succeeded Aristotle in the leadership of the Lyceum. Although personalities such as Galen (Claudius Galenus A.D. 130–200), Ibn Sina known as Avicenna (A.D. 980–1036), Leonardo da Vinci (1452–1519), and Robert Boyle (1627–1691) spent some time speculating on this topic, the major advances in the field of chemosensory research took place in the 20th century, thanks to the development of new instruments and measurement techniques in other fields of science. For example, the invention of oscilloscope in 1922 allowed the earliest extracellular recordings of single-cell gustatory primary afferent nerve activity (Pfaffmann, 1941), while the application of electron microscopy to taste buds in the 1950s revealed the presence of microvillae instead of cilia, as was hypothesized by biologists of that era. From a technological point of view, the pioneering work of Persaud in 1982 (Persaud and Dodd, 1982) opened up new prospects to instrumentally reproduce human basic sensorial functionalities by means of an array of partially selective sensors and pattern recognition techniques. This powerful approach mimics what actually happens in living beings, where recognition of many thousands of different odours and tastes is obtained by means of a much smaller number of receptors (Buck, 2005). The main interest in the development of the so-called electronic noses and tongues comes from the request of low cost, high throughput, versatile pseudo-analytical instruments capable of replacing expensive and inefficient human panels in the assessment of products (food, beverage, packaging, etc.), as well as to lower the cost of selected urine and blood tests, to serve as screening for medical diagnosis, and to monitor the quality of the environment.

So far, much more attention has been paid to the development of electronic noses compared to electronic tongues. For the latter, most reports in literature are based on classic electrochemical methods, such as potentiometry, voltammetry and conductimetry (Ewing, 1985).

* Corresponding author. Tel.: +39 050 2217056; fax: +39 050 2217051.
E-mail address: giovanni.pioggia@ing.unipi.it (G. Pioggia).

0956-5663/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.bios.2006.10.031

Potentiometry is the direct application of the Nernst equation through the measurement of the potentials of non-polarized electrodes with no current flowing. The potentials depend on the nature and concentration of the ionic species in solution as well as on the medium and the type of electrodes; theoretical values can be determined for simple systems based on thermodynamic considerations (free energy variations). Most research in this field is devoted to the development of suitable electrodes. Semi-permeable membranes of various types have demonstrated varying degrees of selectivity and specificity suitable to be combined with pattern recognition techniques (Winquist et al., 2000; Hayaschi et al., 1995). Application areas include health care (urine analysis) and food analysis (Hayaschi et al., 1995; Toko, 1996). Solid-state potentiometric sensors have been used for the detection of heavy metal ions (Vlasov et al., 1997), while chalcogenide glass membranes have been reported for food analysis and environmental monitoring (Di Natale et al., 1997; Legin et al., 2000; Vlasov et al., 2000).

Voltammetry allows the study of the composition of an electrolytic solution by plotting its current/voltage characteristics. In the usual procedure, the current flowing between two electrodes is measured when a varying potential is applied to one of them (the polarizable electrode, the other is the reference electrode kept at a fixed potential). Different information is obtained by changing the voltage waveform (ramp, pulse, etc.), the amplitude or the working electrodes. This method often combines a high sensitivity with a poor selectivity, so most work is also in this case devoted to the development of specific working electrodes. Good results for the classification of various types of drinking water, milk and other beverage have been obtained with metal electrodes (Krantz-Rülcker et al., 2001; Winquist et al., 1997).

Conductimetry is the direct measurement of conductance between two inert identical electrodes, so that most specific effects due to electrodes are eliminated. This method is often used in combination with the former, since the information obtainable is limited (Krantz-Rülcker et al., 2001).

An interesting approach that diverges from electrochemistry was proposed by Lavigne et al. (1998). Resin beads were derivatized with a variety of indicator molecules and the absorption properties (red, green and blue light intensities) monitored by means of a charge-coupled device. The system was responsive to Ca^{2+} ions at various pH.

The use of impedance spectroscopy in e-noses and e-tongues is almost unknown. Riul et al. (2003) measured the capacitance of conducting polymers at 1 kHz, and found the sensors capable of taste detection. In fact, impedance measurement is often considered a slow and unnecessarily accurate method for repeated and rapid electrical measurements, and is more often used for preliminary characterization of complex circuits.

In this paper, an electronic tongue prototype based on the impedance measurement of a composite sensor array is presented. Five different sensors were fabricated comprising three different recognition mechanisms: a carbon nanotube (CNTs) loaded hydrogel, two commercial polymers loaded with carbon black and two conducting polymers. Since their discovery in the early 1990s, CNTs have been intensively investigated for their actuating, mechanical and sensing properties. As far as chemical sensing is concerned, it appears that the carbon side wall of the nanotubes is amphoteric in nature and interacts weakly and non-specifically with several chemical species (Tsai et al., 2003; Trojanowicz, 2006). CNT array based sensors have been reported for gas detection (Dai et al., 2002). In these systems, the wide band chemical response of nanotubes is reduced by the use of chemoselective coatings such as carbosilanes and methacrylates (Snow et al., 2006). Carbon black on the other hand is more inert in comparison, and in sensors is mainly used for rendering non-conductive compounds electrically conductive to facilitate signal transduction (Sisk and Lewis, 2006). Five compounds with different chemical characteristics (a carbohydrate, two salts, a weak organic acid, an amino acid) were chosen as a simple case study for their capability of eliciting different kinds of gustative perceptions. Sensor responses to these compounds (glucose, sodium dehydrocholate, sodium chloride, citric acid and glutamic acid) were characterized in a wide concentration range over a period of 4 months.

2. Experimental methods

2.1. Materials

2.1.1. Suspension 1

A 80:20 (v/v) blend of 10 g/ml polyvinyl alcohol (PVA, MW 30,000–70,000, Sigma–Aldrich) in water and 1 g/ml polyallylamine (PAA, Sigma–Aldrich) in water was prepared. Sixty milligrams per milliliter of single walled carbon nanotubes (a gift from Ray Baughman) in dimethylacetamide (DMA, Fluke) were sonicated, and a 1:1 (v/v) blend of PVA:PAA and the CNTs solutions was obtained by dropwise addition (CNTs to the polymer solution) and 5 min of sonication. The resulting suspension 1 contained about 0.6% weight of CNTs, and was used to prepare the sensor 1.

2.1.2. Suspensions 2 and 3

Polylactic acid (PLA, MW 300,000, Boeringher-Ingelheim) was dissolved in chloroform to obtain a 10 mg/ml solution (solution A). Carbon black was sonicated in benzene in two different concentrations, 10 and 50 mg/ml (solutions B and C, respectively). Suspension 2 was obtained by sonicating A and B in an 80:20 (v/v) ratio, while suspension 3 was a sonicated blend of 80:20 (v/v) A and C. Suspensions 2 and 3 were used to realise sensors 2 and 3, respectively.

2.1.3. Suspensions 4 and 5

The synthesis of poly(3,3′-dipentoxy-2,2′-bithiophene) and poly(3,3″-dipentoxy-2,2′:5,2″-terthiophene) has been described in previous papers (Zotti et al., 1995; Gallazzi et al., 2003). Chemical doping of polymers, i.e. direct reaction with an oxidizing salt, was carried out by dissolving 10 mg of polymer in a 1:1 trichloroethylene/chloroform mix, then adding a doping solution of 2.6×10^{-2} M iron perchlorate in acetonitrile. The molar ratio of polymer to salt was 3:1. The resulting suspension went through ultrasonic stirring for 3 min, during which it turned from dark pink to dark blue. Sensor 4 was made from suspension 4 containing poly(3,3′-dipentoxy-2,2′-bithiophene) and sensor

5 was made from a suspension containing poly(3,3″-dipentoxy-2,2′:5,2″-terthiophene). These sensors were reconditioned by immersion in a saturated solution of sodium dodecyl-sulfonate for several hours. The reconditioning by immersion in a saturated solution of sodium dodecyl-sulfonate was necessary because a continuous increase of resistance was observed after the immersion of the sensor in water. This was attributed to the diffusion of low molecular weight dopant ions (ClO_4^-) through the polymer matrix into the solution. After treatment with sodium dodecyl-sulfonate, which is more resistant to diffusion, the resistance value remained stable for the subsequent months of use.

2.2. Sensor fabrication

The sensor support plates were a 21 mm × 4 mm × 0.6 mm alumina plates containing two vacuum evaporated gold electrodes 1 mm width, 15 mm length, 400 μm inner gap and 2 μm thickness to allow impedance measurement (Fig. 1). Sensors 1–3 were fabricated by depositing 1 μl of suspension on the support plates and heating for 90 min at 75 °C until a stable value of dc resistance was obtained. Sensors 4 and 5 were fabricated by depositing 1 μl of the corresponding suspension on a sensor support plate and letting the liquid medium evaporate until a uniform coating polymer layer was obtained. A sixth sensor composed of the alumina plate and the bare electrodes was also added to the array as a reference.

2.3. Data acquisition

The electric impedance of the sensor array was monitored at a frequency of 150 Hz. At much higher frequencies, the impedance converges to a single value independent of the sensor composition and only related to the conductivity of the system, whereas at lower frequencies the system is slow and subject to ambient noise. The slope of the impedance spectrum at around 150 Hz is maximum, and this frequency was thus selected as the most sensitive, capable of guaranteeing the best discrimination. An automated measurement system composed of an impedance meter, a mechanical arm, a rotating platform and a data acquisition card was designed and realised. The rotating platform was capable of housing six beakers, which were filled with five solutions and the rinsing deionised water. A multiplexer allowed the sequential scanning of the sensors for the impedance measurement, while the array was automatically dipped into the baseline and test solutions by the coordinated movements of mechanical arm and rotating platform. The whole device was controlled by a PC equipped with a data acquisition electronic board (National Instruments PCI6023E) and running a software developed in the Labview environment. A power supply generates a 150 Hz sinusoidal voltage which is sent to a $V \longrightarrow I$ converter. The converter outputs a constant current (the stimulus) that flows in a reference resistance and in the sensor. The resulting voltage at the two ends of the reference resistance is collected by a differential amplifier and is later used as the reference voltage. Another differential amplifier collects the voltage at the two ends of the sensor, which will result in a signal with different module and phase with respect to the reference voltage. The analog signals Port1 and Port2 are then converted, acquired and processed.

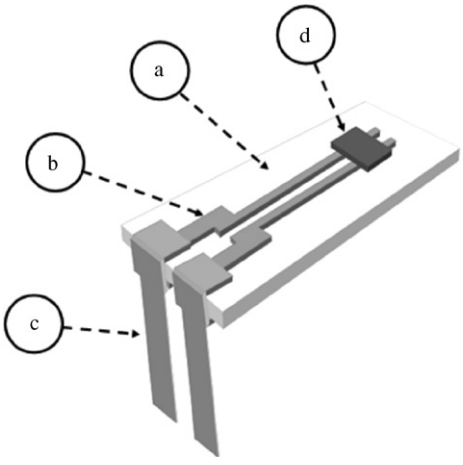

Fig. 1. Sensor layout: (a) alumina substrate; (b) gold contacts; (c) pins; (d) sensing layer.

2.4. Measurement protocol

The response of each sensor to the five compounds eliciting different tastes (bitter, sweet, umami, salty, acid) was characterized over a wide concentration range (two decades), and comprised the range of human sensitivity. Ten solutions were prepared for each compound using the concentrations shown in Table 1. The following protocol was adopted:

(a) Sensors in air, start of data acquisition;
(b) Sensors dipped in distilled water;
(c) Sensors in air;
(d) Sensors in solution 1;
(e) New cycles (a)–(d) for the other solutions;
(f) Sensors in air, stop acquisition.

At the end of this run of measurements, 36 values of both modulus and phase were acquired for each solution relevant to air (16 data), distilled water (10 data) and solution (10 data). For each compound and for each concentration 6 series of measurements were carried out with 10 solutions of increasing concentration, in all 30 randomly ordered series.

3. Results

The composite array based system was subject to two different measuring modalities. The first for the purpose of sensor characterization is here reported, the second to test the arrays capability of discriminating solutions in a concentration range typical of human foods is reported in Part II (Pioggia et al., 2007). The mean values and standard deviations of some of the results obtained are summarized in Figs. 2–5. Conductivity and pH values were also measured for each solution and are also shown in Figs. 2–5. It is clear that the sensors responses are not correlated with conductivity and pH.

Table 1
Solutions under test

	Taste				
	Bitter	Sweet	Umami	Salty	Acid
	Sodium dehydrocholate[a]	Glucose[a]	Glutamic acid[a]	Sodium chloride[a]	Citric acid[a]
C1 (M)	0.0001	0.001	0.001	0.001	0.005
C2 (M)	0.0003	0.0032	0.0032	0.0032	0.0162
C3 (M)	0.0006	0.0055	0.0055	0.0055	0.0275
C4 (M)	0.0008	0.0076	0.0076	0.0076	0.0388
C5 (M)	0.001	0.01	0.01	0.01	0.05
C6 (M)	0.0028	0.028	0.02	0.028	0.14
C7 (M)	0.0046	0.046	0.03	0.046	0.23
C8 (M)	0.0064	0.064	0.04	0.064	0.32
C9 (M)	0.0082	0.092	0.05	0.082	0.41
C10 (M)	0.01	0.1	0.06	0.1	0.5

[a] Compound

It could be argued that the impedance measuring system basically correlates with solution conductivity. Independent measurements were performed with a conductivity meter on the solutions, and, as shown in the figures, the sensor responses do not have any similarity to the responses of the conductivity meter. The sensor responses depend on a complex interplay between solution permeation in the matrix, electromechanical response times and ion affinity/mobility. Each sensor type has a distinct recognition mechanism, with a different dynamic response, and it is this varied array which contributes to the overall discrimination power of the tongue.

From the figures it can be seen that sensors 1–3, which were all based on polymeric matrices loaded with conducting particles, have a wide dynamic range, while sensors 4 and 5, based

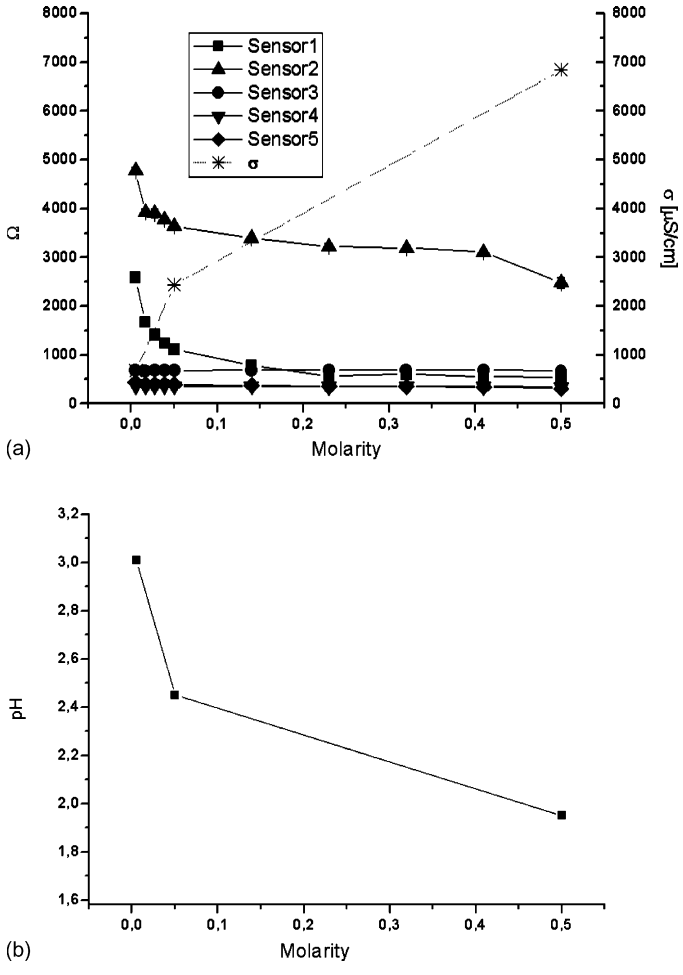

Fig. 2. (a) Moduli of sensor impedances and conductivities of different concentrations of citric acid and (b) pH of the same solutions.

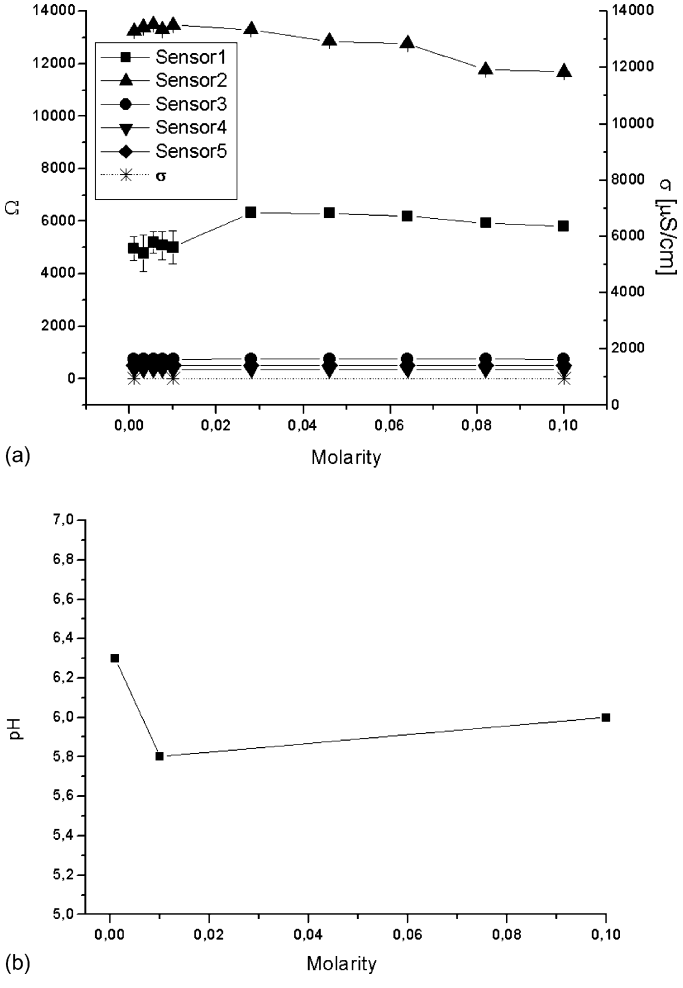

Fig. 3. (a) Moduli of sensor impedances and conductivities of different concentrations of glucose and (b) pH of the same solutions.

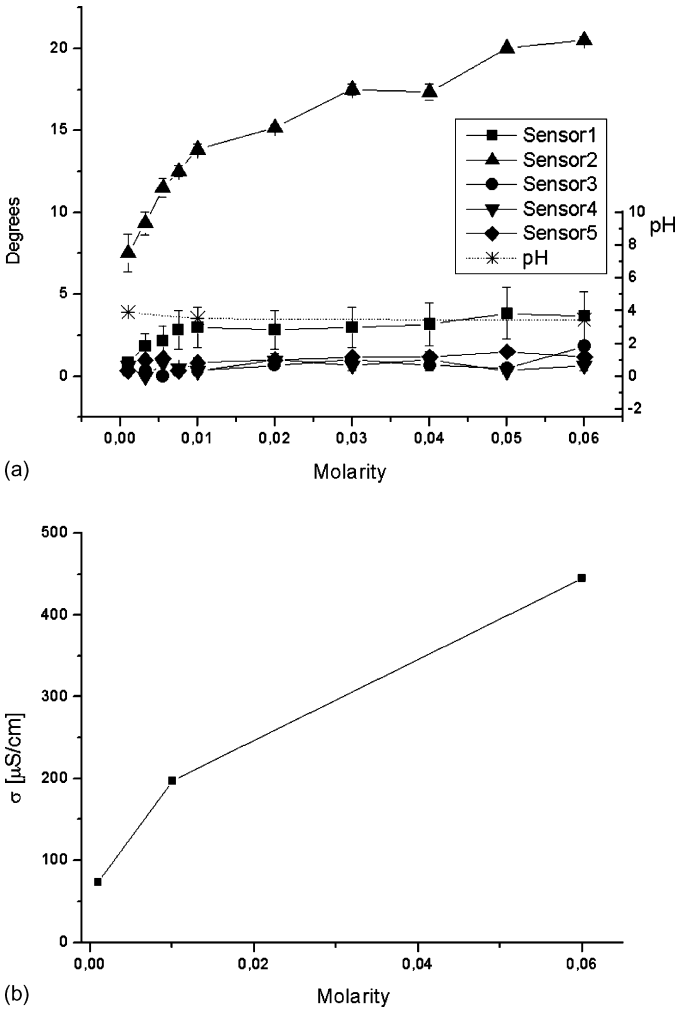

Fig. 4. (a) Phases of sensor impedances and pH of different concentrations of glutamic acid and (b) conductivities of the same solutions.

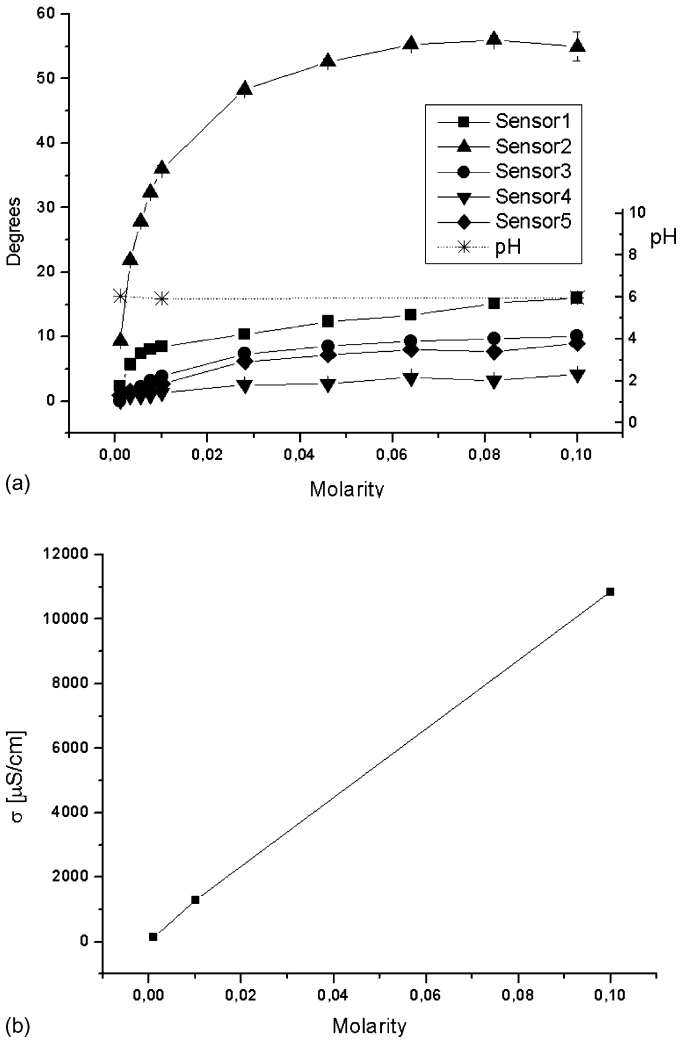

Fig. 5. (a) Phases of sensor impedances and pH of different concentrations of sodium chloride and (b) conductivities of the same solutions.

on conducting polymers, have a flat characteristic that appears poorly selective of both concentration and compound. Of all sensors, sensor 2 (PLA with the lower concentration of carbon black) had the widest dynamic range; phase or modulus changed highly over the range of concentrations tested for all solutions. Sensor 1 (CNT in the hydrogel matrix) was the most repeatable, in that successive measurements were more reproducible with respect to the other sensors. Glucose produces the worst responses of all (Fig. 3); all sensors show very small changes in the values of their moduli (and the same behaviour is observed for the phases, not reported), so it is unlikely that the system will obtain good classification rates for this compound.

4. Discussion

The current research in electronic tongues is based mainly on electrochemical measurements, with the main focus being on the development of novel sensors, such as membranes and electrode coatings. Indeed, the use of impedance measurement represents a novel approach for the realisation of an electronic tongue. This approach is justified by the affinity with the measurement of resistance variations which is the most commonly used method for electronic noses. Our objective is to merge both olfactive and gustative sensing into a human-like taste and smell perception system; the impedance sensing method simplifies the integration process.

A composite array with different materials was used in order to exploit a variety of different sensing mechanisms, and to increase the capability of discrimination between multiple solutes. To realise a composite array, three different sensing layers were investigated. The first sensing layer consisted of a hydrophilic hydrogel loaded with CNTs. A hydrogel is a biphasic material composed of a solid matrix and a permeable liquid phase. The solid reversibly changes its physical properties in response to a change in the properties of the liquid phase such as temperature, pH value, solvent composition, or salt contents. In particular, when a hydrogel with negative charge in the solid matrix is exposed to fluids, a swelling or a contraction according to the presence of negative or positive ions, respectively, can be observed. In the case of a hydrogel with a positively charged solid matrix such a mechanoelectrical transduction is inverted. When a hydrogel is loaded with CNTs, the system is rendered electrically conductive. CNTs also increase its tensile strength

and it is likely that they contribute to the entrapment of soluble moieties through non-specific chemisorption. In this work the hydrogel solid matrix consisted of a blend of poly(vinyl-alcohol) (PVA) and polyallylamine (PAA) loaded with CNTs. PVA forms a hydrophilic hydrogel which shows high tensile strength and elongation before breaking. Its adhesive properties, resistance to solvents and ease of functionalization make it of great interest for chemical and biological sensing. The addition of PAA allowed the addition of positive charge to the matrix through a thermally induced cross-linking reaction. In this way, the gel matrix was rendered more selective to negatively charged moieties. Other polymers with different charge may be also used in order to differentiate the selectivity of the sensor.

The second sensing layer was realised from a matrix of polylactic acid (PLA) loaded with carbon black and it is based on the method described by Lonergan et al. (1996). Carboxyl groups are present with in the PLA matrix and may be charged in aqueous conditions rendering it more selective to permeation of positively charged species. The presence of dissolved ions and molecules in contact with and adsorbed into the porous polymer matrix produces changes in its electrochemical properties according to the concentration, permeability and degree of affinity of each single analyte. According to Lonergan et al. (1996), the critical factor is the permeation of the solute into the polymer, and it is this which gives rise to variations in electrical impedance.

In the third case, a sensing layer consisting of poly(alkoxybithiophenes) previously used to detect organic vapours (Gallazzi et al., 2003), was adopted. In alkoxy-substitute polythiophenes, the change of the electrical resistance is related to a change of the amount and/or distribution of the charge carriers following the chemical or chemical–physical change in the polymer phase brought about by a surface and bulk interaction between conducting polymer matrices and test solution.

Sensor 1 (CNTs in hydrogel) was the most repeatable, while sensor 2 (PLA with carbon black) had the widest dynamic range. The conducting polymer sensors performed rather poorly in all measurements. In sensors 1–3, the conducting substance as well as the carrier matrix is different, and the individual components which contribute to sensor performance are therefore difficult to identify. As far as the carbon black loaded sensors are concerned, the lower mass fraction of carbon black in sensor 2 with respect to sensor 3 renders it more sensitive to the presence of substances capable of altering the electrical impedance because of the reduced number of conduction pathways present in the matrix. This behaviour was also recently observed by Sisk and Lewis (2006).

5. Conclusion

We have demonstrated the feasibility of using electrical impedance to monitor the response of an array of sensors to a number of different liquids. A novel aspect of this work is also the use of an array of sensors composed of different materials and with different response mechanisms. To verify the reproducibility and repeatability of the sensors, an extensive number of tests was randomly repeated with all sensors over a long time period. The composite sensor array was shown to be robust and capable of responding to the tests with various solutions. We were also able to identify the best sensors, which were all based on polymeric matrices loaded with conducting particles; the conducting polymer sensors were far less sensitive.

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