Towards a Conducting Polymer-based Electronic Nose and Electronic Tongue

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ABSTRACT

An integrated system has been designed for detection of gas, volatile liquid and liquids based on the concept of an electronic nose and an electronic tongue. The detection mechanism relies on the changes in electrical resistance that occurs when an array of microelectrodes, coated with conducting polymers, is exposed to different samples. The data collected from such resistance changes has been processed by an artificial intelligence trained computer in conjunction with pattern recognition data analysis to identify and quantify the chemicals of interests. Detection of pH and sodium chloride was considered as case studies for the electronic nose and tongue applications respectively. This integrated artificial intelligence/electronic nose and tongue can be further developed to detect colour (electronic eye) for display device applications.

Key Words: electronic nose, electronic tongue, computer modeling, conducting polymer

INTRODUCTION

Conducting polymers are being extensively studied and used in a wide range of new sensing products.

Polypyrrole and polyaniline, with the chemical structure shown in Scheme I, represent a new class of sensory materials whose unique properties are facilitating the development of intelligent systems [1–3].

The common feature of each of these polymers is the conjugated backbone structure and the stable form being the oxidized macromolecule which produces a positive charge per 2–3 repeat unit [2]. It is important to note that the positive charge on the polymer is balanced by the A^- anion during the oxidation/reduction reaction (Scheme II).

In some cases cation involvement has been reported for charge compensation at the reduction phase. However, for a mobile counterion (this study) anion exchange plays a dominant role in the resistance changes of the polymer [1].

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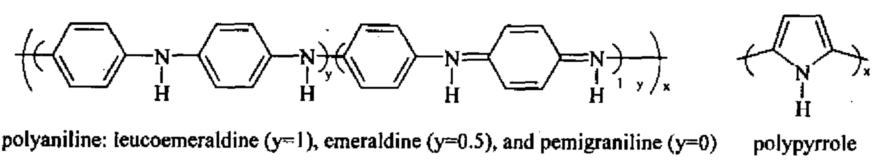
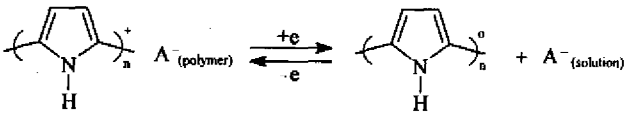


Scheme I. Chemical structures of polyaniline and polypyrrole.



Scheme II. Oxidation and reduction processes for polypyrrole materials with mobile anion.

The A species can be any anion from the simple (e.g., Cl^-) to complex organic anions including polyelectrolytes or even proteins. The movement of anion from polymer to the solution and vice versa is the main feature of the redox switching of the polypyrrole materials. The situation is more complex with polyaniline as the polymer can be protonated and deprotonated by pH changes [4, 5]. Fully oxidized polyaniline can be partially reduced to emeraldine and further reduced to leucoemeraldine with structures illustrated in Scheme I. The beauty of the redox and pH switching of polypyrrole and polyaniline between charged and neutral states is that they maintain their mechanical integrity. This is crucially important for sensing elements. Such unique switching cause changes in the properties, which is the basis of many applications for these materials.

In the course of this paper we present a new and exciting integrated system by which smell and taste can be detected based upon the previous strategies published for detection of salt and pH [6–8]. In this work an integrated system for detection of gases or volatile compounds (electronic nose) combined with detection of solutions, which are responsible for the salty taste (electronic tongue), is introduced.

EXPERIMENTAL

Sensing Approach and Mechanism of Response

Taste

The most sophisticated sensing systems are found in the human body. For example, we can taste via living polymer interfaces. The cellular processes in our tongue are regulated by cell walls comprising dynamic macromolecules that are capable of sensing specific chemical stimuli. Amongst these stimuli chemical stimuli are of our interests.

There are two types of chemical sensory systems that use different receptors and process information at different locations in the brain. Taste [1], in which the receptors are specialized sensory cells and smell [2] or olfactory, where the receptors are neurons Raven and Johnson [9].

Taste receptors of fishes are the most sensitive chemoreceptors known. The taste receptors, or taste buds, are not located in the mouth, as in human, but rather are scattered over the surface of the body of fish. These taste buds are exquisitely sensitive to amino acids, A catfish, for example, can distinguish between two amino acids at a concentration of less than 100 micrograms per liter. The ability to taste the surrounding water in this way is very important to fishes enable them to sense the presence of food in an often murky environment.

One group of chemoreceptors in human being is also concerned of special taste buds, but not as sensitive as in fishes. The taste buds in human beings are located in the mouth (Figure 1). Each taste bud is associated with an afferent neuron. Humans have four kinds of taste buds, each of which responds to a broad range of chemicals. The stimuli to which different kinds of taste buds respond are salty, sweet, sour, and bitter. Our complex reception of taste is composed of

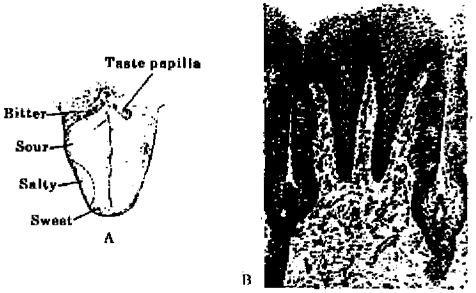


Figure 1. (a) Four kinds of taste buds located on different regions. (b) Individual taste buds are bulb-shaped collections of chemicals receptor cells that open out into the mouth through a pore [9].

different combinations of impulses from these four types. The chemoreceptors are concentrated on different parts of the tongue, sweet and salty at front, sour on the sides, and bitter at the back (Figure 1a).

Learned from the human tongue our approach is to develop a dynamic sensing electrode by which we are able to detect solutions, which contain salt such as sodium chloride (a salty-taste solution). Detection of sodium chloride and other salts have been already reported using a sandwich electrode [5, 10]. The salty taste is related to type of salt and its extent depends on the concentration of the salt in the operational solutions. This approach can be used in the food industry to control the extent of salty taste in the products if it is combined with a computer (when an artificial neural network package was used) for on-line data processing and prediction.

A typical example of off-line salt detection ($CaCl_2$, LiCl and NaCl) is reported in Table 1. The table consists of data numbers from 156 to 160 for three different salts used in this study. The first row of the table indicates the number of data presented to the network as inputs and outputs. The other rows are part of the collected data during the experiments. As the table shows, for the selected 160 inputs there are outputs considered as data Nos. 161-163. Since the network cannot deal with letters, the outputs are classified in ones and zeros.

Smell

Humans smell by using olfactory receptor cells located in the lining of the nasal passage (Figure 2). The receptor cells are neurons. The process of smell in humans is the same as the sense of taste in fishes while the chemoreceptors in the process of smelling in human are surrounded by air rather than water.

Using the design shown in Figure 3 we demonstrated the capability of the system to detect pH. A conducting polyaniline was used and the detection of

Table 1. (a) Typical input data presented to the computer for modeling and pattern recognition experiments. Due to the nature of the software used the type of the salt was introduced to the computer in digital form (combination of 0 and 1). (b) Output prediction by computer.

. . .	156	157	158	159	160	Ca	Li	Na
. . .	–0.09	–0.09	–0.09	–0.09	–0.10	1	0	0
. . .	–0.11	–0.09	–0.10	–0.10	–0.11	0	1	0
. . .	–0.10	–0.10	–0.10	–0.11	–0.10	0	0	1

(a)

Salt	Output 1	Output 2	Output 3
Na	–0.01768	–0.11035	0.95254
Ca	1.011793	0.073661	–0.10175
Li	–0.00987	0.98108	0.00729

(b)

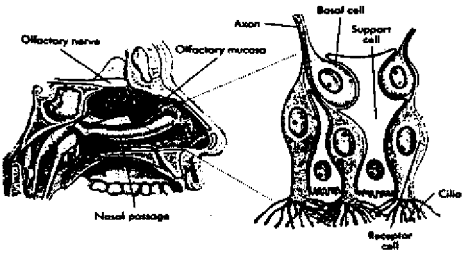


Figure 2. The human nose structure.

pH was considered as an output signal. The unpleasant smell of solutions such as NH_4OH with having volatile vapor (ammonia) can be detected via the use of a polyaniline film. The smell of gas samples can be also detected if they are flown over the polymer from a pressurized cylinder after being combined with nitrogen as an inert gas.

Before the nose can be used, it must first be taught to recognize differences in different samples. This Involves many repeated trials in which the air above the commercial samples is sent past an array of sensors. This changes the electronic signals they produce in a particular way. The signal is recorded by the computer and becomes a small part of a data set. Using fuzzy logic the computer will eventually learn to distinguish different samples based on the information in its data set, and can then be used to produce a quick and accurate analysis of the product. An example of pH measurements of the polyaniline materials, using an off-line computer modeling, while basic and acidic solutions were used is illustrated in Figure 4.

By applying a small DC potential (by power supply) and measuring the current (by meter) the resistance of the polymer is calculated [10]. It is necessary to mention that for high conductive materials the system of two-probe (used in this study) is not an appropriate method. However, if polyaniline is used as partly oxidized and partly reduced form the two-probe method is a feasible one. The basic pH detected by our sensor is related to the concentration of ammonium hydroxide and indirectly to the odor of ammonia.

It is important to note that there are other chemicals like H_2SO_4, H_2S, HNO_3, HCl and NaOH which are able to cause some changes in polyaniline resistance as soon as they are in vicinity. However, with calibration curve it is possible to separate the resistance changes due to only ammonium [11]. This is the basis of an electronic nose that has been explained in more detailed in the next section where an on-line computer modeling and output prediction is

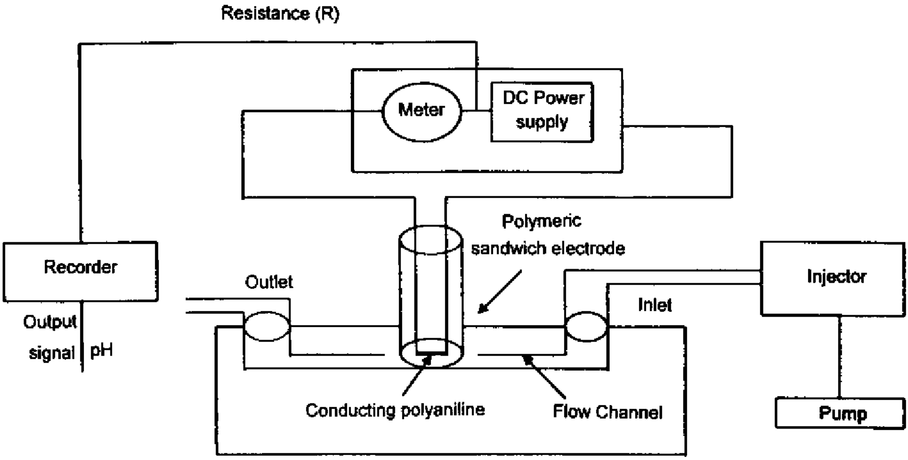
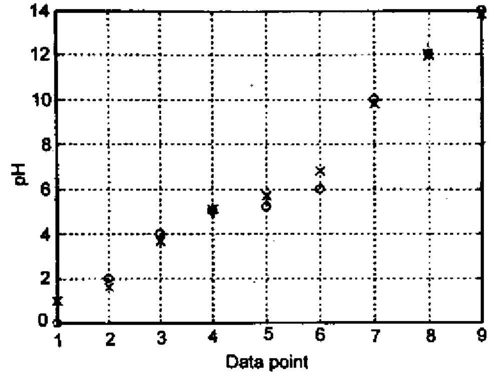


Figure 3. Schematics of the flow injection cell used for pH detection and detection of the odor of ammonia.



o and x are real and predicted pHs, respectively.

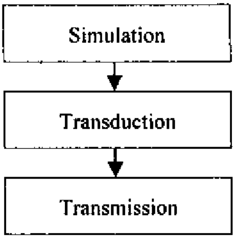
Figure 4. Off-line computer prediction of pH.

discussed.

Integrated Electronic Tongue and Nose

To detect the taste or/and the smell of samples electronically and in an on-line/real time manner, the use of an array of microelectrodes and the on-line involvement of a pre-trained computer to our design are essential. The use of the array enables us to produce different sensing electrodes coated with polypyrrole, polyaniline and their composites. It has been experienced that the use of the composite could result in more reproducible pH detection [12] that is the basis of our new electronic nose. The computer in our design acts the same as the brain in our body.

The path of sensory information to the brain in human being is composed of three elements as shown in Scheme III:



Scheme III. The path of sensory information.

– Stimulation: A physical stimulus impinges on a neuron or an accessory structure, called a sensory receptor.
– Transduction: The sensory receptor initiates the opening or closing of ion channels in a sensory neuron.
– Transmission: The sensory neuron conducts an action potential along an afferent pathway to the central nervous system.

All sensory receptors are able to initiate nerve impulses by opening or closing ion channels within sensory neuron membranes. They differ from one another with respect to the nature of the environmental input that triggers this event. Broadly speaking, three classes of environmental stimuli have been recognized as shown in Table 2. Receptors capable of responding to these stimuli, singly or in concert, constitute the sensory parts.

All the input from sensory neurons to the central nervous system arrives in the same form. To the brain, every arriving impulse is identical to every other one. The information that the brain derives from sensory input is based on the frequency with which these impulses arrive and on the neuron that transmits the input. If the auditory nerve is artificially stimulated, the central nervous system perceives the stimulation as a noise. If the optic nerve is artificially stimulated in exactly the same manner and degree, the stimulation is perceived as a flash of light. To recognize sensory input to the nervous system, one must examine the source of sensory signals, as well as factors that influence the frequency with which these sources send nerve impulses to the brain.

The organs we use to taste and smell are sensitive to a wide range of compounds and each microsensor in our tongue and nose produces different patterns. Our brains have learned to distinguish these

Table 2. Classes of environmental stimuli.

Mechanical forces	Chemical	Electromagnetic energy
pressure	taste	light
gravity	smell	heat
sound		electricity
touch		magnetism

patterns and identify a huge number of very specific fragrances.

The integrated electronic tongue and electronic nose is designed to do the same thing. An array of sensors is used to achieve the selectivity necessary to reliably distinguish different smells and tastes. This array of microelectrodes is connected to a powerful and already trained computer as shown in Figure 5 and Figure 6 for solutions and gas samples, respectively.

The end result is an overall impression from a variety of sensory input. The information from each polymer sensor is then fed into the microprocessor that acts like our own brain in creating a final analysis and result. The device mimics the human sense of smell and taste to assess the quality of samples, and test for contaminants before being smelled or tasted by humans. The trick is teaching the computer to recognize the data as different chemicals as explained in Table 1. This can be achieved by using fuzzy logic [13, 14], statistical method [15, 16], artificial neural network [17], clustering [18, 19] which are powerful artificial intelligence based tools used in the computer modeling and pattern recognition applications.

Using this device in the food industry the taste and smell of chemicals such as vinegar and lemon can be detected by measurement of the pH of the samples since acetic acid and citric acid can be detected. It could tell the maturity of wine as well.

This integrated system, if reliably tested in real

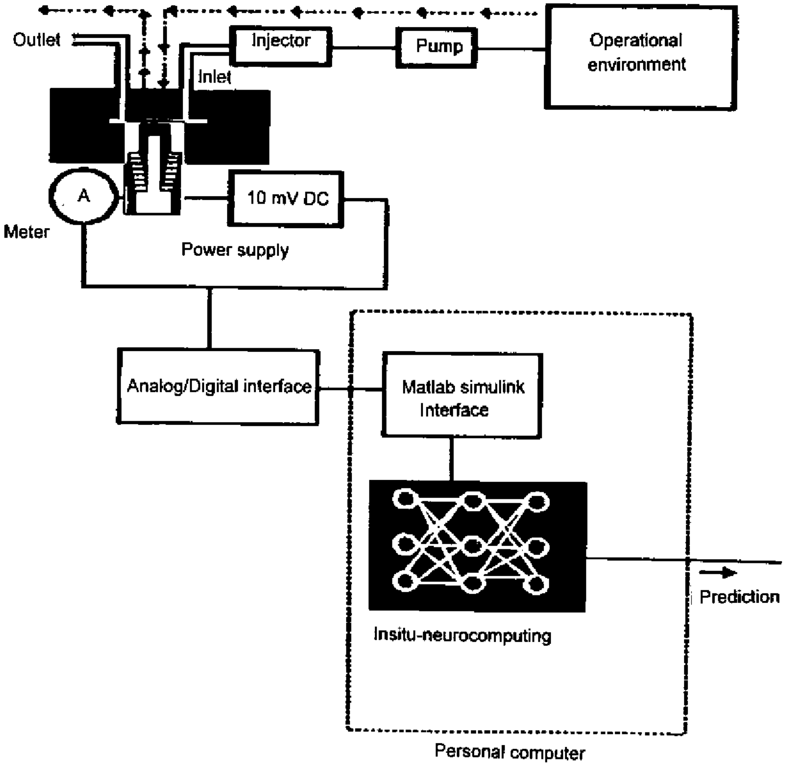


Figure 5. An integrated device with capability of sniffing volatile gases and tasting different liquid samples. An array of microelectrodes is connected to a power supply for resistance measurements.

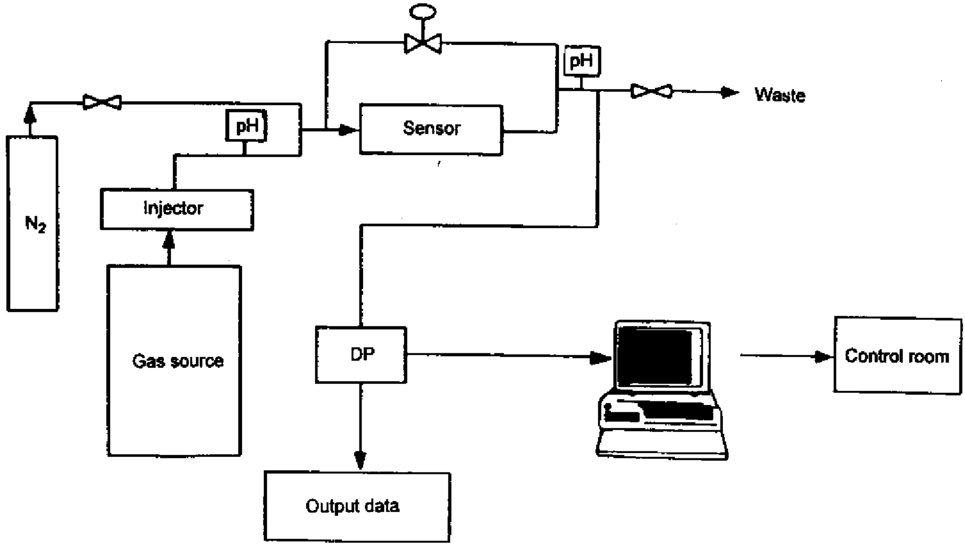


Figure 6. A chart of an integrated device with capability of sniffing various gas samples. The same array as in Figure 5 is used. The quantity and quality of output can be also controlled based on the processed data.

environments, can be a breakthrough as it potentially by passes the traditional methods of quality testing. Moreover, it can prevent us being poisoned through direct smell or taste of the unknown gases and solutions. With further studies an electronic eye can be combined with this new design based upon colour changes properties of the conducting polymers, which makes this study even more challenging.

CONCLUSION

An integrated electronic tongue and electronic nose has been developed with the potential applications of detection of the taste and smell of lemon, vinegar, wine and also unpleasant odor such as ammonia. The system uses an array of microelectrodes as sensing element on which different conducting polymers are coated. The system is combined with powerful artificial intelligence methods as the main decision making section. The computer acts the same as our brain to recognize the pattern based upon the received data.

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