Miniaturized Potentiometric Sensors Based on pH-Dependent Polymers

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In recent years, there has been a growing interest in electrodes chemically modified with electropolymerized films and in their application as potentiometric pH sensors since the protonation of nitrogen or oxygen atoms in the polymers are expected to impart a pH response to the modified electrode. If glass membrane electrodes are still the most often used pH sensors, the polymer-based pH electrodes have many advantages compared with traditional glass membrane pH electrodes. For example they can be miniaturized and so be useful for clinical or biological applications such as *in vivo* analysis.

Thus, our purpose is to elaborate pH sensors using electropolymerized polyethylenimine (PEI) and polypropylenimine (PPI) modified electrodes since we developed a new way of synthesis that allows us to coat surfaces with a thin film of PEI or PPI [1] by electropolymerization of different di or triamines. Moreover these polymers are good candidates as transductors since:

- they are strongly bonded to the electrode surfaces during the electropolymerization step,
- thanks to the presence of the amino groups onto the modified surfaces the polymers are pH-dependent,
- these films grow thick enough because of their non-conducting properties,
- they give high impedance to the modified electrodes providing a better protection to interferents,
- they are insoluble in water and in main organic solvents.

These chemically modified electrodes were successfully tested as pH sensors in buffered solutions. Indeed, the responses of the sensors to pH changes were linear, reversible and stable in time over a period of 30 days (Figure 1) for the pH range between 3 and 10 [2]. The effect of the thickness of the polymer films was also studied.

Then we miniaturized our pH sensors to promote a commercial application [3]. These miniaturized analytical sensors (Figure 2) were fabricated using photolithography, a batch and inexpensive fabrication process. This method allowed us to pattern metal electrodes on an oxidized silicon surface. Then a sputtering technique was chosen to deposit the platinum film on the patterned electrodes. Next, one electrode was coated with a polymer film when the other one was coated with silver to be used as reference electrode (Figure 3). Finally, a detection system was designed which allows us to obtain the pH value in Volts since Liquid Crystal Display is used to display either the voltage or the pH value.

PEI films can be used for *in vivo* applications since PEI is biocompatible, so we have also developed potentiometric urea biosensors based on PEI and PPI. These biosensors are enzymatic, that is why we have tested 4 different enzyme immobilization methods. The most efficient potentiometric biosensors is the one using adsorption followed by reticulation with glutaraldehyde as enzyme immobilization method.

PEI film electrodes can finally be used for the detection of glucose [3], ammonia [4] or heavy metal ions detection since their potentiometric responses versus the concentration of Ni^{2+} and Cu^{2+} is linear until a thresold concentration [5].

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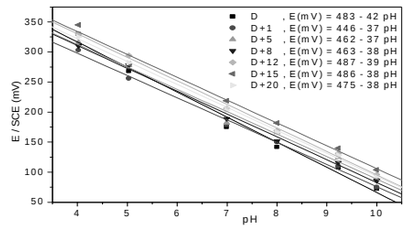

Figure 1: Potentiometric Responses to pH Changes of a pH Sensor

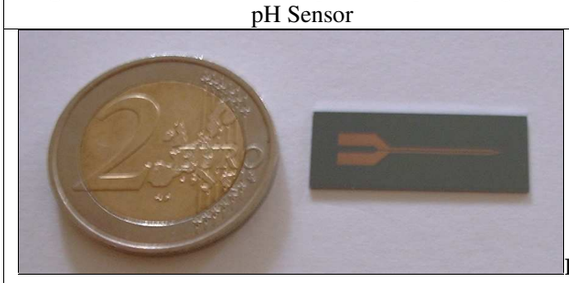

Figure 2: Photo of a pH Sensor