POLYMERIC FILM SENSORS BASED ON PAH-PAZO IONIC SELF-ASSEMBLED MULTI-NANOLAYERS

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Abstract: A sensor platform composed by interdigitated electrodes covered by a tailored nanofilm of 5 bilayers of PAH and PAZO polyelectrolytes was successfully built and tested in NaCl solution at relative low concentrations (10^{-5}-10^{-6} M). The effect of temperature on the electrical measurements was addressed and indicated its importance for to sake accuracy reduction in about one order of magnitude. The film morphology was studied by using ellipsometry and atomic force microscopy techniques. The first inferred precise and consistent values for the film thickness about 50 nm. With respect to the second, relative low values of the surface roughness of about few nanometers were measured and also micrometer diameter agglomerates and channels with a bilayer size depth were identified.

1 INTRODUCTION

Sensing, monitoring, and control are natural tasks performed by any living organism and also an increasing part of the humankind activity in which technology is directly or indirectly involved in day-to-day life. Numerous sensors are constantly being developed and the advent of the nanomaterials increases even further their variety and applicability.

A new branch of potential platform for sensors is being widely researched by using polyectrolytes nano-thin films ionically self-assembled in bilayers via what is so-called layer-by-layer (LbL) technique (Decher and Hong, 1991, Oliveira Jr., 2001). The production of a bilayer involves sequential adsorption of two opposite charged polyelectrolytes from an aqueous solution, one by one, onto an inert substrate such as glass or metal. The process is repeated for attaining multi-layers. This simple and inexpensive technique is also expected to deliver films with high thermal stability and robust to critical solvent and alkaline environments which are the ideal platform for sensors.

Among several polyeletrolytes bilayer pairs for building this platform, the ones made by the polyanic poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamide]-1,2-ethanediyl, sodium salt] (PAZO) and the polycationic poly (allylamine hydrochloride) (PAH) have a great potential and results have already been reported (Mermut and Barrett, 2001 and Ferreira, 2007).

In addition, *selective* molecules (organic, inorganic, enzymes, DNA, etc) can be equally *mobilized* onto the last layers in order to react chemically to a particular analyte of interest.

The interplay of a broad set of parameters related to the measurement such as the temperature, pH, hysteresis, and their time-domain dynamic (drift) should be carefully quantified aiming to control or more likely to correct theirs effects via *a posteriori* software analysis. This optimization towards reliability can enhance the enormous commercial potential of the LbL sensors mainly as a monitor in an environment with no lab-control.

This work reports preliminary results on the temperature effects on a LbL film sensor plataform built with PAH/PAZO bilayers and tested in rather simple aqueous solutions containing sodium choride (NaCl) via impedance spectroscopy technique. The polyelectrolytye PAZO which is at the last surface of the multilayers should attract electrostatically the cation Na^+, so the global electrically properties of the multilayer are expected to change according to the concentration of this cation and therefore NaCl concentration is sensed. In addition to this, preliminary analysis on the sensor film thickness and morphology are presented by using ellipsometry and atomic force microscopy (AFM) techniques.

2 EXPERIMENTAL

The sensor was produced from polyelectrolytes LbL films deposited onto substrates of BK7 optical glass where gold interdigitated electrodes were deposited by vacuum evaporation. The sensor effective area was about $2x5mm^2$, the interspace between the lines was 20μm and their width and thickness were 2μm and 0.2μm, respectively. These dimensions were measured by a Dektak perfilomoter and an optical microscopy Olympicus SZ-PT.

The polyelectrolytes poly [1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) and the poly(allylamine hydrochloride)(PAH) (average M_w= 50,000-60,000g/mol) were acquired from Sigma-Aldrich. The PAH polyelectrolyte aqueous solution with concentration of 10^{-2} M was prepared by dissolving this polyectrolyte in deionised water with a resistivity of 18.2MΩcm supplied by a Millipore system (Milli-Q, Millipore GmbH). The PAZO aqueous solution also with a concentration of 10^{-2} M was obtained by dissolving this polyelectrolyte on an aqueous buffer solution of pH=10. The polyelectrolyte concentrations were based on the molecular weight repeat unit and the buffer solution was prepared mixing a 0.05M sodium hydrogen carbonate ($NaHCO_3$) aqueous solution with a 0.1M

sodium hydroxide (NaOH) solution in a proportion of 500:107(v/v) (Ferreira (a), 2007). The PAZO solution was also filtered with a 5 mm thick and 50 μm porous diameter ceramic filter.

The LbL films were prepared by immersing the substrate with the interdigitated electrodes into the PAH solution for 5 minutes, washed 3 times into water for a total of 10s, and then immersed into the PAZO solution for the same 5 minutes and equally washed but into the buffer solution instead of water. This procedure leads to a production of a bilayer and repeated until the 5 bilayers were obtained. Finally, the thin film was dried with a nitrogen flux.

The sensor impedance measurements were carried out by a Precision Impedance Analyser Agilent 4294A (40Hz-110MHz, 1mHz resolution, GPIB connection). The root mean square oscillator voltage signal level was 50 mV.

The film thickness was measured using a spectroscopic ellipsometer model HORIBA Jobin Yvon UVISEL. A three layer model was used assuming the sensor is composed by a film layer on the top of a 1 mm thick BK7 glass substrate and another on its back. The spectral range used was 1.5-6.5 eV (531-2302 nm) with a 0.025 eV increment.

The AFM measurements were performed by a Dimension 3100 SPM with a Nanoscope IIIa controller from Digital Instruments (DI) under ambient conditions in tapping mode[TM]. A commercial tapping mode etched silicon cantilever probe from DI (constant force of 42N/m, resonance frequency of 320kHz) and a 90x90 μm² scanner were used. The scan rate was 1.51 Hz. The image resolution was fixed to 256×256 pixels.

3 RESULTS AND DISCUSSION

The influence of the NaCl concentration on the sensor impedance ($Z=Z'+iZ''$) were analysed. Real (Z') and imaginary (Z'') parts, module and phase of Z, and Nyquist representation were all studied. The clearest way for visualise that influence was by using the Z' part against the impedance analyser frequencies which is presented in the graph of fig.1. The sensor was immersed into solutions of different NaCl concentrations from the lowest concentration, virtually null corresponding to Milli-Q pure water, to the highest of 1M. Impedance spectra measurements within several weeks show systematic drifts for all concentrations but not to a point to overlap any two consecutive values, excepted at low frequencies below 5 kHz.
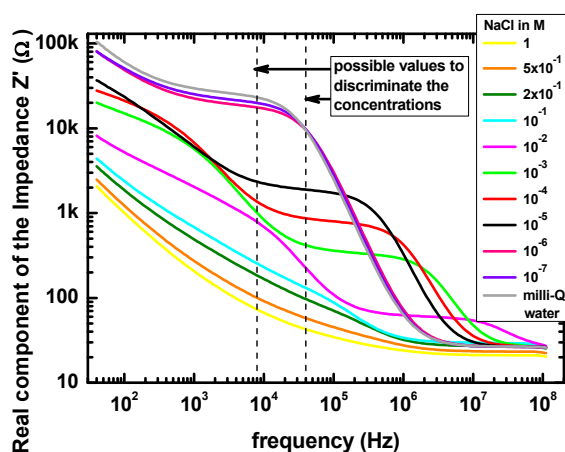
Figure 1: Real part, Z′, of the sensor impedance versus the impedance analyser frequencies for the sensor immersed in NaCl aqueous solutions with different concentrations.
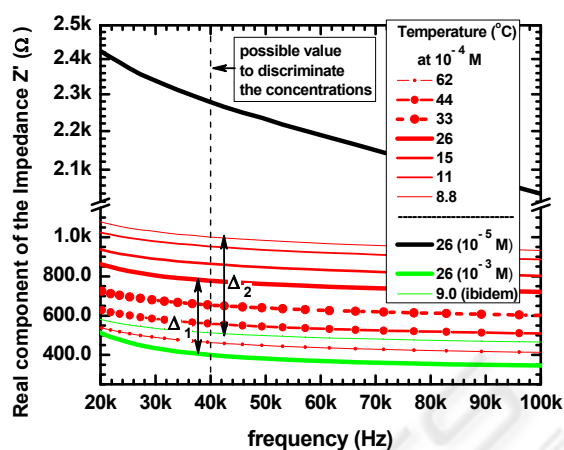

Figure 2: The real part, Z′, of the sensor impedance versus the impedance analyser frequencies for the sensor immersed in NaCl aqueous solutions with few different concentrations and temperatures.

The overall Z′ curves show a complex behaviour with the frequency and concentration leading to a short window for an effective analysis which is empirically delimited (e.g. by the two lines drawn in this figure). In the lower limit at 8kHz, a concentration up to 10^{-5} M can be easily measured and possibly 10^{-6} M too if sufficient statistics and at least temperature measurements of the aqueous medium are available as will be seen further on.

At the upper frequency of 40 kHz the sensor is robust since the Z′ values are well distinguished for each concentration, in addition to be less sensitivity to the frequency. Values of 10^{-5} M can not be really exceeded. However, in this region the sensor thermal stability is very high as it is shown in the plot of fig.2, where the impedance spectra are shown for NaCl solutions of 10^{-4} M and 10^{-3} M concentrations over a temperature range of 9 to 62°C and 9.0 to 26°C, respectively. Around 40kHz, Z′ variation is almost the same for temperatures close to 9°C (Δ_2) or to 26°C (Δ_1) for these concentrations. However, it is clear that the 10^{-4} M concentration can be mistaken for the 10^{-3} M if the right temperature curve is not used. An overlap of these curves occurs below 20kHz, even for small temperature variation.

Therefore, the possibility to measure lower concentrations (e.g. down to 10^{-6}M) really demands the precise knowledge of the temperature and the statistical values of the concentration in a laboratory environment. A more feasible alternative to this might be to increase the sensor sensitivity by increasing the number of bilayers, for example.

Ellipsometry measurements inferred a precise and consistent sensor film average thickness of 49±4nm. The ellipsometric measurements were

carried out about 8 mm away form the interdigitated electrodes where only the PAH/PAZO film deposited onto the glass substrate was presented.

Topography measurements of the PAH/PAZO films were obtained by AFM scanning over the film sensor at 2 mm and 8 mm away from the interdigitated electrodes, again in regions where only the PAH/PAZO film deposited onto the glass substrate was presented. In the fig.3 two typical 3-D reconstructions of the topography, both with a scan window of 5x5μm², are presented in a sensor used in a NaCl aqueous solution. In the fig.3a, a relative smooth surface is observed except for the presence of agglomerates with a micrometer size diameter and at least 60 nm height. These structures are possibly made or a result of NaCl attachment to the surface. The root mean square roughness (Rrms) varied over 7-13nm for this type of scan window. These values further reduce to 3-4nm for scan windows of 1×1μm². In the fig3b, clear channels were shown at the surface possibly due to the effect of the electrical currents, since the electrical field created was relatively high, i.e. of the order of 2.5kV/m. The creation of such structure should be avoided in order to keep the multilayer integrity and thus the sensor reliability. A worthwhile attempt to minimise this might be the reduction of oscillator voltage applied by the impedance analyser. In addition, the reduction of the upper frequency could also help since no useful information can be extracted for values much beyond the optimum frequency (by 40kHz in this case) where Z′ substantially reduces and the current flow through the sensor increases accordingly.

The channels depth can be roughly estimated as 10nm from the topographic AFM measurements

shown in fig.3b. This corresponds to the size of one bilayer assuming a linear scaling between the number of bilayers with the film thickness.
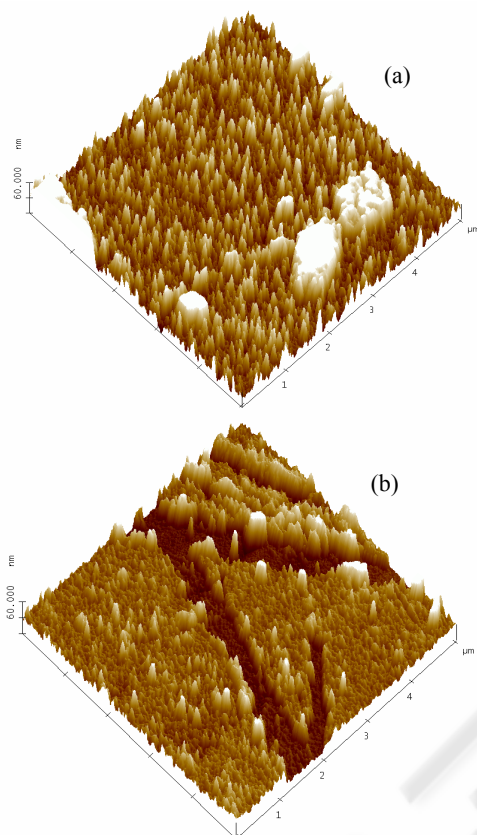

Figure 3: AFM 3-D topography of the PAH/PAZO film: (a) in a typical region; (b) where channels were formed.

As a remark, the AFM morphology of samples that have not been immersed into a NaCl aqueous solution showed no agglomerates such as the ones discussed earlier and their Rrms values are lower, regardless the scan window values used, i.e. they are 3-5nm, 1.5nm, and 1.6nm for $5\times5\mu m^2$, $2\times2\mu m^2$, and $1\times1\mu m^2$, respectively. The particular value of 1.6nm here is about one magnitude smaller from that of ~13nm, obtained from previous studies (Ferreira, 2008). This indicates that filtering the polyetrolytes solution such as for the PAZO here may play an important role for reducing the roughness.

4 CONCLUSIONS

A sensor platform composed by an interdigitated electrode covered by a tailored film of 5 bilayers of polyelectrolytes PAH-PAZO was successful built and tested in NaCl aqueous solutions at relative low concentrations around few micro moles per litre.

The effect of temperature on the impedance measurements was addressed in a limited range of this variable. Nevertheless, the preliminary results indicate that the knowledge of this parameter is vital for attaining accuracy close to one order of magnitude in useful range of concentrations.

The film thickness and morphology were characterized by using ellipsometry and atomic force microscopy techniques. The first allowed to obtain precise and consistent values for the multilayer film thickness of about few tens of nanometers. From the second, relative low values of surface root mean square roughness, about few nanometers, were measured and channels with a bilayer size depth and micrometer diameter agglomerates were also identified.

ACKNOWLEDGEMENTS

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