POLYANILINE – MORPHOLOGY AND SENSING PROPERTIES

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Abstract

The adsorption process of dye on polyaniline films electrodeposited on niobium has been investigated using electrochemical impedance spectroscopy. The negative □G°_{ads} value (-35.802 kJ mol^{-1}) and high value of K_{ads} obtained in our measurements indicate that Amino Black 10 adye adsorption process is spontaneous with the formation of a stable adsorbed dye layer on the polyaniline surface. The adsorption takes place via a combination of physical and chemical adsorption.

Keywords: PANI, dye, EIS

Introduction

In the last years Polyaniline (PANI) benefit from special attention due to its special properties and practical applications. It is an inimitable polymer because presents many oxidation forms (the polymer is in fact a mixture of different oxidation states: leucoemeraldine- pale yellow, emeraldine-green and conductive, pernigraniline- dark violet) and it conducting form is stable in air or water.

PANI properties depend on the synthesis conditions and can be obtained in different morphologies such as plate-like and leaf-like structures nanoflakes, nanofibers, nanotubular, nanospheres. The tendency of PANI to aggregate depends on the experimental conditions. Microstructures such as flower-like and leaf-like structures at pH 7, rod-like and granular-like morphologies at pH 3 and 1 or mushroom-like morphology were reported in literature. Also, 3D structures composed of nanosheets, nanorods based microspheres or nanorods based microrods have been observed in alkaline solution synthesis. The electrochemical method allows a more rigorous control of synthesis parameters and offers a very convenient way to study the electrochemical properties of PANI nanofibers [1-3]. Electrochemical impedance spectroscopy (EIS) is a noninvasive method for determining the fractional coverage of the adsorbed monolayer and investigates the nature of adsorption of some analytes on the PANI surface

The scope of our work was to investigate the nature of adsorption of Amino Black 10 dye (AB10) on the PANI. EIS was chosen as measurement technique to investigate the interaction between the dye and the PANI surface.

Material and Methods

Aniline was freshly distilled under reduced pressure and stored in dark at low temperature. Double distilled water and analytical grade sulphuric acid were used to prepare the electrolyte solutions.

PANI films were obtained by electrochemical polymerization of aniline on niobium substrate from H_2SO_4 solution as reported [3]. The potentiodynamic polymerization was performed in a

standard three-electrode electrochemical cell connected to an Autolab PGSTAT 302N. The working electrode was a Nb disc (A = 1 cm^2), two graphite rods were used as counter-electrodes and a saturated calomel electrode (SCE) as reference electrode.
EIS measurements were carried out using the FRA Module of Autolab 302N, in the frequency range from 10^6 Hz to 1 Hz and AC voltage amplitude of 10 mV. For each spectrum 60 points were collected, with a logarithmic distribution of 10 points per decade. The experimental electrochemical impedance data were fitted to the electrical equivalent circuit by a CNLS Levenberg–Marquardt procedure using the ZView-Scribner Associates Inc. software.

Adsorption studies

The adsorptions kinetics of AB10 dye was investigated using EIS technique. Adsorption of dye was studied under OCP condition and the adsorption profile was investigated. A dye stock solution of 3×10^{-3} M was prepared by dissolving the dye in distilled water followed by necessary dilutions of this stock solution. The values of surface coverage θ, corresponding to different concentrations of dye have been used to get best linearity isotherm [3, 4]. The values of surface coverage θ were obtained from impedance measurements according to equation (1):

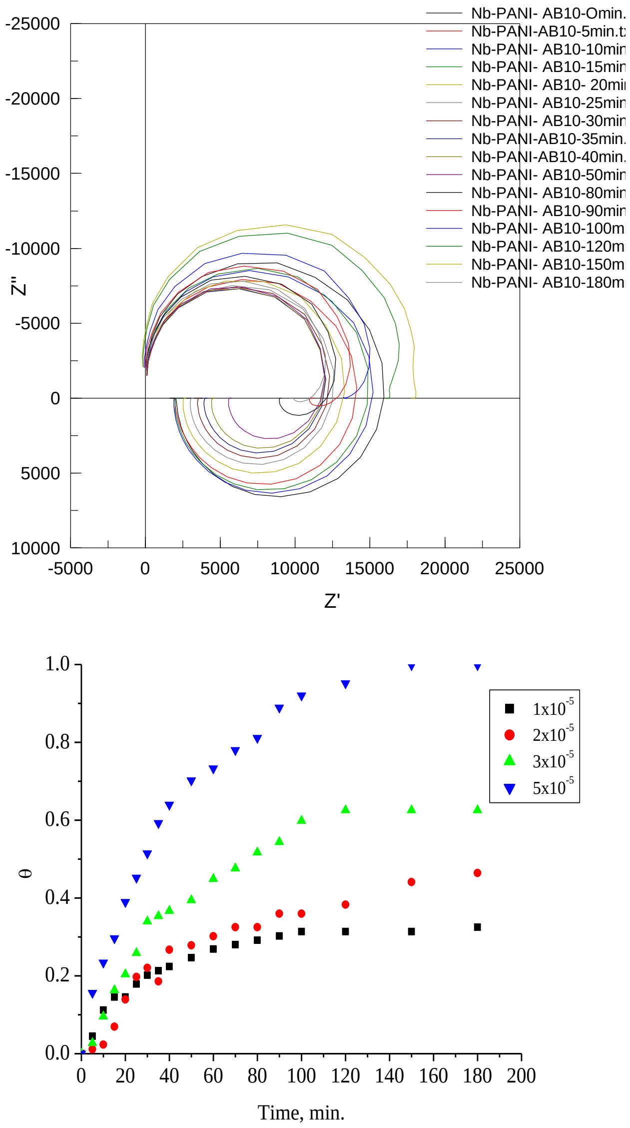
$$\Theta = (C_o - C_i) / C_o \qquad (1)$$

where C_o is the capacitance at time t = 0, C_i is the capacitance at any time.

Results and discussion

For adsorption studies four PANI films were prepared in the same conditions. The deposition of PANI on Nb electrode takes place only after substrate passivation, when Nb is covered by a passivating layer of niobium oxide [17]. The deposition charge *Q* was calculated for each PANI film to verify that they have similar masses and thicknesses. Values of 98, 95, 100 and 98 mC have been obtained for the four PANI films, showing a good reproducibility. The thickness of four PANI films deposited was estimated to be 5.25±0.35 μm using an average density value for polyaniline of 1.4 g cm^{-3} [3]. The spectra of polymer obtained on Nb present the C=C stretching deformation of the quinoid and benzoid rings at 1570 cm^{-1} and 1482 cm^{-1}, the C–N stretching of the secondary aromatic amine at 1293 cm^{-1} [3]. The band at 1372 cm^{-1} present was attributed to the C–N stretching mode in the neighborhood of a quinoid ring. The band at 1232 cm^{-1} is assigned to $C-N^{\bullet+}$ stretching in polaron lattice structure for Pani-Nb. The bands found in the structure of Pani-Nb at 1467, 1448 and 1414 cm^{-1}, was attributed to presence of the phenazine units and the aromatic C–H in-plane bending at 1128 cm^{-1} and the C–H out-of-plane bending at 815 cm^{-1} to the 1,4-substitution of the benzene ring. The vibrations at 780, 725 and 699 cm^{-1} present in the spectra is also a proof of the presence of multi-substituted benzene rings, associated with the formation of branched polymer structures and/or the presence of phenazine-like units. The symmetric stretching vibration of the sulfonate group is observed as a broad band at 1040 cm^{-1} only for Pani-Nb doped state [3]. The morfology of PANI deposited on Nb confirm the formation of network of nanofibers on the surface. The adsorption profile of AB10 dye was investigated by EIS under OCP condition.

The Nyquist plots (Figure 1a) contain depressed semicircles with the center under the real axis. The behavior is characteristic for solid electrodes and is often referred to a frequency dispersion attributed to roughness of the solid surfaces and physical phenomena such adsorption.



a) b)

Figure 1. a) Nyquist plots for PANI/Nb electrode immersed in 1 × 10^{-5} mol L^{-1} dye solution at different moment of immersion and b) the variation of electrode surface coverage in time for all AB10 dye solution concentrations.

The electrochemical electric circuit (EEC) used to model the EIS data include a resistor (R_s is the solution resistance between the reference electrode and working electrode) in series with a parallel connection between a capacitor (double layer capacitance), Cdl expressed as a constant phase element CPEdl (used instead a pure capacitance to account for the non-ideal capacitive response from the interface) and a resistance (R_{ct} is the charge transfer resistance). In EIS spectra the inductive loop appeared at low-frequency values (LF) was attributed to the relaxation process of dye species adsorbed on the PANI electrode surface and was modeled by elements R_L (is the inductive resistance) and L (is the inductance) [5, 6]. The *C*dl values result after fitting of EIS data show an increase with increase of the concentration of dye in solution. The adsorption lead to a decrease in the local dielectric constant and/or to an increase in the thickness of the electrical double layer as water molecules present at the PANI-electrode interface are replaced through adsorption phenomena. [6]. When adsorption becomes significant the disappearance of the inductive loop is observed (Figure 1a) also R_L was observe to be proportional to the surface coverage of

PANI with AB 10 molecules. The value of L was found to decrease as a consequence of the accumulation of dye molecules in the porous PANI layer. The values of θ were obtained using capacity values determined by fitting EIS data with EEC and calcultating according to equation (1). The evolution of surface coverage of PANI in time is presented in Figure 1b. In the first minute the adsorption is rapid, 85-90% of PANI surface is covered by the dye molecules. After 60 minutes the adsorption became slower and reaches a plateau. The rate of absorption process was evaluated from the decay of electrode capacitance in the first moments when an irreversible layer of dye is considered to be form on the PANI surface. The proper model for adsorption kinetics was establish to be the Langmuir model (equation 2) which gave a better fit for the representation of ln(1- *Θ)* against time.

$$\Theta(t) = [1 - e^{-k_a t}] \qquad (2)$$

The k_a was 18.21 ± 2.56 × 10^{-3} s^{-1}. These results are similar with the results reported for the azo red dye adsorbed on PANI surface [6].
The Langmuir adsorption isotherm fit the experimental data (equation 3a) and the K_{ads} was found to be 34005.21 mol^{-1}.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3a) \qquad R_L = \frac{1}{1 + K_{ads} C} \quad (3b)$$

where θ is the surface coverage, C is the dye concentration, K_{ads} is the adsorption equilibrium constant The values obtained for slopes in the Langmuir model were less than unity and indicate the existence of interactions between the adsorbed dye molecules and PANI surface. The dimensionless separation factor, $R_{Langmuir}$ are less than unity for all concetrations, confirming that the adsorption processes on PANI are favorable. Based on the value obtained for K_{ads} the free energy of adsorption (ΔG^o_{ads}), was calculated using the equation (4):

$$\Delta G^0 = -RTLn(55.5 K_{ads}) \quad (4)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature in Kelvin, K_{ads} is the adsorption equilibrium constant, ΔG^o_{ads} is the standard free energy of adsorption, 55.5 is the concentration of water in the solution in mol dm^{-3}.
The negative ΔG^o_{ads} value (ΔG°_{ads} = -35.802 kJ mol^{-1}) and high value of K_{ads} obtained indicate that adsorption process is spontaneous with the formation of a stable adsorbed of AB10 dye layer on the PANI surface. The adsorption takes place via a combination of physical and chemical adsorption but mainly due to physical adsorption. The ΔG^o_{ads} value for the adsorption of AB10 dye on PANI/Nb is closer to the value reported for the adsorption process of red azo dye onto PANI/Nb (ΔG^o_{ads} of -36.381 kJ mol^{-1}) [6].

Conclusion

The PANI film deposited electrochemically on Nb surface present a high specific surface and presents dye retaining capacity. The proper model for AB10 dye adsorption kinetics was establish to be the Langmuir model and k_a was $18.21 \pm 2.56 \times 10^{-3}$ s^{-1}. The Langmuir isotherm describes well the adsorption phenomena. The change of Gibbs energy evaluated for the adsorption of AB 10 dye onto PANI/ Nb electrode presents a negative value (-35.802 kJ mol^{-1}). The ΔG^o_{ads} value and the high value of K_{ads} propose that adsorption process is spontaneous with the formation of a stable adsorbed dye layer on the PANI surface. The adsorption of AB10 dye takes place via a combination of physical and chemical adsorption.

Acknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are acknowledging Romanian Academy for financial support in the frame of Programme 2/2018 from ICT. This work is dedicated to the Centennial Anniversary of ROMANIA.

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