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A Study on a Phase Transition in Electrodeposited Thin Film Polyaniline Using AC Conductivity Measurements*

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Ac conductivity – temperature dependencies of Au/polyaniline/Au structures with the electrodeposited thin film polyaniline are presented. The data for the reduced and reversibly oxidized polymer samples of estimated thickness being in 10^{-1}–10^{0} µm range are shown. The charge transport laws are found similar to that observed for the chemically prepared conducting polymer. The observed crossover in the conductivity – temperature dependence coincides with the increase in the electrical capacitance of the polyaniline electrode reported earlier.

Key words: polyaniline, thin films, electrochemical deposition, ac conductivity, cyclic voltammetry

Conducting polymer – polyaniline can be obtained by chemical or electrochemical oxidation of aniline [1]. The later method is well suited for deposition of the polymer on many electrode materials, metals and semiconductors, to form layers of controllable thickness and porosity. Under an electrochemical control, electrical conductivity of polyaniline can be switched between high and low values in a reversible manner. A partially oxidized, conducting polyaniline can be reduced reversibly to a semiconducting state. Many cycles of the switching can be performed with a high stability in the electrochemical characteristics of the polymer.

Polyaniline (PANI) belongs to a group of the mixed electronic-ionic conductors. The nature of ionic dopants affects considerably the electric properties of the polymer. A substrate electrode/polymer system is called the polymer electrode and can be useful in many applications, including sensors and power sources. Recently, the double layer and redox capacitances of the secondary polyaniline electrodes in aqueous trichloroacetic acid were studied in great details using electrochemical impedance spectroscopy (EIS) [2]. Three processes resulting in relatively high electrical capacitances of the electrodes were revealed in the frequency range from 0.1 Hz to 50 kHz. The capacitances depend on the oxidation state of the polymer. Moreover, the temperature dependencies of the double layer and redox capacitances of the polyaniline electrodes seem to indicate that polyaniline may undergo a phase change at temperatures

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≥ 298 K. To confirm this hypothesis calorimetric and dielectric spectroscopy measurements on electrochemically prepared thin layer samples of polyaniline were undertaken. It would be also of interest to compare the characteristics of the electrode-posited films to relevant data on chemically synthesized polyaniline, already reported in the literature.

Preliminary studies of the thin film polyaniline electrodes under dry conditions, *i.e.* without a contact with a liquid electrolyte but with a possible trace water presence in the film, will be presented in this communication. Temperature and frequency dependencies of the electrical conductivity of Au/PANI/Au systems were examined using dielectric spectroscopy in the temperature range between 150 K (–123°C) and 325 K (+52°C), at frequencies from 100 kHz to 20 MHz [3]. We are aware of numerous conductivity data for polyaniline samples. However, this does not concern the samples of submicrometer thickness that can be easily prepared electrochemically. The DSC results will be invoked for a comparison and cyclic voltammetry (CV) for a polymer state testing.

EXPERIMENTAL

Polymer film preparation: The polyaniline electrodes were obtained by electropolymerization of aniline on Au electrodes in aqueous solutions containing hydrochloric acid and aniline. A detailed protocol of the procedure differed from case to case but its essentials were much the same, i.e. a potentiodynamic control of the electrolysis with a more positive oxidation potential at the very initial stage of the polymer deposition, corresponding to the nucleation and an early stage of a new phase growth; other details can be found elsewhere [4]. Stationary or rotating Au electrodes of diameter 0.5 cm were used. Thicknesses of the deposited polyaniline layers were in the range of 10^{-7}–10^{-6} m. They were estimated based on the charge involved in the reversible redox switching of the polymer, as described in [4]. Four samples were prepared for the dielectric spectroscopy measurements: Au/PANI$_{ox}$(0.42 μm), Au/PANI$_{red}$(0.42 μm), Au/PANI$_{ox}$(2.2 μm) and Au/PANI$_{red}$(0.38 μm). The numbers in brackets indicate thicknesses of the polymer layer. The red and ox indexes indicate the reduced and oxidized states, respectively. The electrode was rotated only during preparation of the Au/PANI$_{red}$(0.38 μm). The samples were dried in stream of nitrogen and stored in air at room temperature between measurements.

AC conductivity measurements: The conductivity measurements for the Au/PANI electrodes were done *ex-situ*, in a temperature range between 130 and 330 K. Temperature was changed linearly with a rate of 1 K/min. Gold plates were used to make electrical contacts to the samples. AC conductivity, σ_{ac}, was measured by means of a HP 4285A Precision LCR Meter in the frequency range between 75 kHz and 20 MHz with 20 mV input signal amplitude. The measurements were performed assuming the simple parallel equivalent circuit shown in Figure 1.

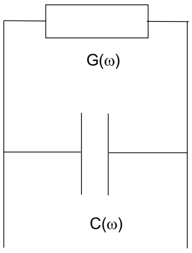

Figure 1. Equivalent circuit used for dielectric spectroscopy measurements.

In this model, G(ω) is the electrical conductance and C(ω) is the electrical capacitance. The both model elements are considered frequency dependent. Relation between G and conductivity σ is following:

$$G = \sigma \cdot s/d$$

where s is the area and d is the thickness of the polymer.

CV tests of chemical stability of the polymer: Redox reversibility of polyaniline film electrodes was used as a measure of chemical stability of the polymer submitted to dielectric measurements. Relevant tests were performed before and after dielectric spectroscopy measurements using cyclic voltammetry. Stationary voltammograms (the 3rd cycle ones) of polyaniline were recorded for <–0.1V, +0.6V> (the electrode potentials in the SCE scale) potential range, starting at the oxidized state of the polymer. The electrolyte solution was 1M HCl and the potential scan rate was 0.100 V/s. Only one couple of reduction-oxidation peaks is expected for the reversible switching of polyaniline under these conditions. No traces of polyaniline decomposition products were observed in the voltammograms. Integration of the voltammograms gives values of electric charges involved in the reversible switching that served as a measure of the chemical stability of polyaniline under experimental conditions. A typical behavior is shown in Figure 2.

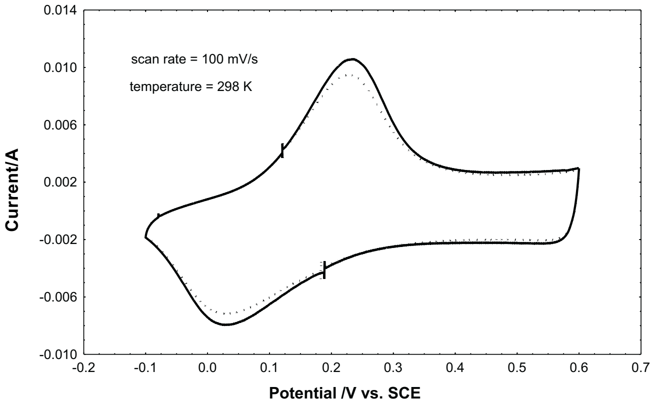

Figure 2. Cyclic voltammogram of Au/PANI(d = 0.42 μm) in 1 M aqueous HCl solution; line – before DS measurements; dots – after DS measurements. Other parameters indicated in the Figure.

A slight decrease in the CV currents recorded after dielectric spectroscopy (DS) measurements can be assigned to a loss of the active material due to the mechanical manipulation of the sample. Nevertheless, no change in the CV curve of the redox switching was detected.

RESULTS AND DISCUSSION

A goal of our measurements was to find tendencies in the temperature and frequency changes of ac conductivity for electrodeposited polyaniline films. The values of σ_{ac} for most samples can be only roughly estimated due to uncertainty in the s and d values. Nevertheless, we can expect that the σ_{ac} values are undoubtedly greater than 0.005 S/m in the whole temperature range, the limit value being typical for a semiconductor. Furthermore, in a large part of the temperature range investigated, the conductivity of the oxidized polymer increases on heating, which is a typical behavior for insulators and semiconductors. The representative conductivity data for the oxidized and reduced PANI samples of various thicknesses are collected in Figure 3.

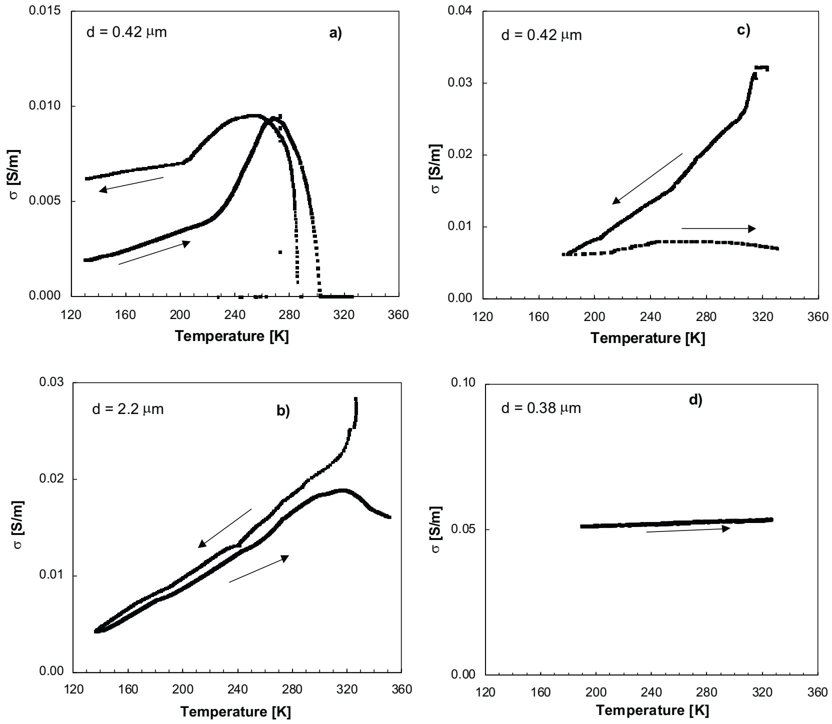

Figure 3. The conductivity – temperature dependencies of four studied samples; a,b) the oxidized PANI, c,d) the reduced PANI. Thickness d indicated in the Figures.

It should be noted that in the investigated frequency range (100 kHz–20 MHz) σ_{ac} was frequency dependent (*i.e.* σ_{ac} decreased with frequency) and negative values of the capacitance C(ω) were observed. The behavior might be ascribed to artifacts of DS measurements for the well conducting samples. As the ac conductivity is predicted to be greater than the dc conductivity [3], the observed opposite frequency dependence of σ_{ac} was ignored. Therefore, the data were analyzed using models of dc conductivity, thus assuming a predominant contribution of the dc component to the measured conductivity of the polymer.

Differences in the $\sigma \sim T$ dependencies for PANI films of different thickness are clearly visible from the selection in Figure 3. A crossover to the metallic sign of the conductivity – temperature dependence is observed for the oxidized polymer samples. However, the behavior differs in details for the two oxidized samples. The main difference between the oxidized and reduced states is that the oxidized polyaniline exhibits a maximum of σ_{ac} in an ambient temperature range (270–320 K). The behavior is reversible, *i.e.* is observed for the reverse temperature scan, and then a hysteresis of the location of the maximum conductivity is seen. Those features might have indicated a phase transition in the polymer phase. However, no anomalies on the DSC curves were found, either for cooling or for heating scans in this temperature region.

The “red” samples of the polyaniline show only slightly lower conductivity value, which is practically independent of temperature. The enhanced value of the conductivity on cooling for the sample with thickness 0.42 μm may be related to a water content.

The electric properties of a chemically synthesized polyaniline were studied by Diaz Calleja and Matveeva using dielectric spectroscopy [5]. Dependencies of dielectric losses and susceptibility of the polymer as the functions of temperature (170 K, 370 K), electric field frequency (0.3 Hz–30 kHz) at 1 V ac voltage amplitude were interpreted as due to water molecules that act as a doping impurity similar to acid anions. Our measurements fall into a similar temperature range. The ac perturbation parameters are quite different. However, the maximum observed in the ac conductivity vs. temperature might be related to a water content as well. Nevertheless, a temperature range of the observed maximum of ac conductivity coincides with the features found for the electrochemical capacitances [2].

An attempt to describe quantitatively the conductivity vs. temperature dependence was undertaken for the oxidized polyaniline sample (see Figure 3a). Relevant functions considered for the dc conductivity in heterogeneous organic polymeric systems were used to approximate the experimental data [6,7]. The functions were as follows:

$$\sigma = \sigma_0 \cdot \exp[-(T_0/T)^n] \tag{1}$$

with $n = 1$, $1/2$ or $1/4$ and $T_0 > 0$.

The equation (1) with different values of n corresponds to different physical models of charge transport in conducting polymers that results in the semiconductor-like conductivity – temperature dependencies [6–9]. Usually, the combined conduction laws, with n between 1/4 and 1, can be observed in the real materials. On the other hand, the quasi one-dimensional metallic conductivity, as for example in the case of defect free, homogeneously doped polyacetylene chain, is described by the following dependence [7,9]:

$$\sigma = \sigma_0 \cdot \exp[+(T_0/T)^n] \tag{2}$$

with $n = 1$ and $T_0 > 0$.

A statistical analysis of the experimental data was done according to the logarithmic form of equations (1) and (2), that is:

$$\ln\sigma = a + b \cdot T^{-n} \tag{3}$$

where: $\sigma_0 = e^a$, $T_0 = (-b)^{1/n}$ for (1), and $T_0 = (b)^{1/n}$ for (2).

Therefore, the $\ln\sigma = f[(T)^{-n}]$ dependencies for the oxidized PANI sample were linearized for three temperature ranges (“low” <155–200 K>, “middle” <230–260 K> and “high” <275–290 K>). Results of the analysis are collected in Table 1, which includes the usual measures of goodness of the given approximation, *i.e.* correlation factor (R-coeff.) and sum of squared deviations ($\Sigma(\sigma_i)^2$), in its last two columns.

Table 1. Results of the conductivity – temperature dependence analysis for the oxidized PANI(d = 0.42 μm) sample, according to the equations indicated on the right hand side of the Table. The temperature ranges described in the text.

Temperature range	n	Scan	σ_o /Sm^{-1}	T_0/K	$\Sigma(\Delta\sigma_i)^2$	R^2-coeff.	
Low temperatures	1	heating	$1.351\cdot10^{-2}$	$2.743\cdot10^{2}$	$7.740\cdot10^{-9}$	0.9993	$\sigma = \sigma_o\exp[-(T_o/T)^n]$
		cooling	$8.910\cdot10^{-3}$	$4.799\cdot10^{1}$	$9.102\cdot10^{-10}$	0.9996	
	1/2	heating	$6.439\cdot10^{-2}$	$1.715\cdot10^{3}$	$3.196\cdot10^{-9}$	0.9998	
		cooling	$1.207\cdot10^{-2}$	$5.842\cdot10^{1}$	$1.655\cdot10^{-9}$	0.9992	
	1/4	heating	$1.463\cdot10^{0}$	$2.679\cdot10^{5}$	$1.181\cdot10^{-9}$	0.9999	
		cooling	$2.217\cdot10^{-2}$	$3.454\cdot10^{2}$	$2.460\cdot10^{-9}$	0.9988	
Middle temperatures	1	heating	$1.760\cdot10^{0}$	$1.374\cdot10^{3}$	$1.427\cdot10^{-7}$	0.9992	$\sigma = \sigma_o\exp[-(T_o/T)^n]$
		cooling	$5.905\cdot10^{-2}$	$4.313\cdot10^{2}$	$7.100\cdot10^{-8}$	0.9977	
	1/2	heating	$4.868\cdot10^{2}$	$3.092\cdot10^{4}$	$1.642\cdot10^{-7}$	0.9991	
		cooling	$4.325\cdot10^{-1}$	$3.435\cdot10^{3}$	$9.164\cdot10^{-8}$	0.9972	
	1/4	heating	$3.721\cdot10^{7}$	$6.255\cdot10^{7}$	$2.009\cdot10^{-7}$	0.9989	
		cooling	$2.320\cdot10^{1}$	$8.720\cdot10^{5}$	$8.106\cdot10^{-8}$	0.9969	
High temperatures	1	heating	$4.133\cdot10^{-5}$	$1.487\cdot10^{3}$	$4.102\cdot10^{-8}$	0.9950	$\sigma = \sigma_o\exp[(T_o/T)^n]$
		cooling	$3.648\cdot10^{-4}$	$7.251\cdot10^{2}$	$3.142\cdot10^{-8}$	0.9902	
	1/2	heating	$2.080\cdot10^{-7}$	$3.150\cdot10^{4}$	$4.548\cdot10^{-8}$	0.9953	
		cooling	$3.970\cdot10^{-5}$	$7.854\cdot10^{3}$	$1.342\cdot10^{-7}$	0.9905	
	1/4	heating	$5.230\cdot10^{-12}$	$5.650\cdot10^{7}$	$3.792\cdot10^{-8}$	0.9955	
		cooling	$2.593\cdot10^{-8}$	$7.090\cdot10^{6}$	$2.992\cdot10^{-8}$	0.9907	

Differences in the statistical parameters of the approximations used in our analysis are rather small. Therefore, they cannot be taken as a sufficient criterion for the indication of the transport law. However, from the results collected in Table 1, one can derive a few conclusions: *i*) the semiconductor type σ ~ T behavior can be characterized by equation 1 with an effective n from the range <1/4, 1>; *ii*) the metallic type σ ~ T data give the best fit to equation 2 with n = 1/4. Furthermore, the T_0 parameter that can be related to the activation energy increases with temperature and it is always lower for the cooling scan as compared to the heating scan.

Another function for analyzing the conductivity results can be used as well [8]. Since the reduced activation energy W is defined as follows:

$$W = T\cdot\frac{d\ln\sigma}{dT} = \frac{d\ln\sigma}{d\ln T} \tag{4}$$

using (1) one obtains:

$$W = n\cdot\left(\frac{T_0}{T}\right)^n \tag{4.1}$$

and (2) with n = 1 gives:

$$-W = \left(\frac{T_0}{T}\right) \tag{4.2}$$

Three characteristics can be observed in the case of polyaniline depending on W: a positive W value characteristic of semiconductors, a negative W value characteristic of a metallic behavior, and a W value close to zero, which is characteristic of the critical range between the metallic and semiconducting state. The data shown in Figure 4a correspond to that of Figure 2a (heating scan). The relevant analysis, in log |W| *versus* logT coordinates, is presented in Figure 4b, where a change in the slope from negative to positive values is observed at the temperature of the σ_{ac} maximum. A similar characteristics was reported in the literature for the chemically doped polyaniline samples [8,9]. As representative for the semiconductor type behavior, the negative slope, of value equal n = 0.35, is indicated in Figure 4b.

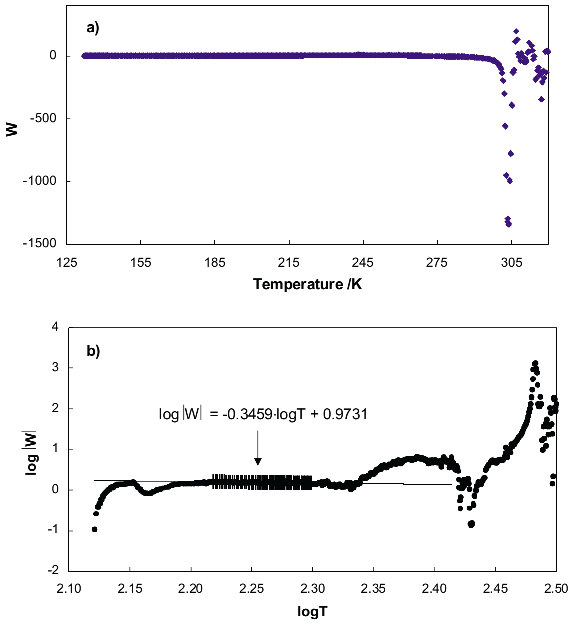

Figure 4. The reduced activation energy W of the oxidized PANI(d = 0.42 μm) sample; a) W *versus* T; b) log |W| *versus* logT, with a linear approximation in a temperature range indicated by an arrow.

The heterogeneous model of the charge transport in conducting polymers is widely accepted [7,10]. Thus, crystallite regions are mixed with amorphous regions, the two types of regions being interconnected or disconnected. The series heterogeneous model results in an overall electric resistivity which is a sum of the two contributions, so the total resistance is dominated by the more resistive amorphous regions [10]:

$$\sigma^{-1} = (g_1\cdot\sigma_1)^{-1} + (g_2\cdot\sigma_2)^{-1} \quad (5)$$

where g_i's are coefficients dependent on dimensions of the contributing regions (*i.e.* geometrical factors). The crossover in the conductivity – temperature dependence is governed by the temperature dependencies of conductivities of the contributing regions and values of their g-coefficients. The crossover temperature of our polyaniline samples occurs at rather high temperatures, *i.e.* in a room temperature range. It might indicate a relatively high value of the conductance of the metallic domains (*i.e.* the crystallite regions) and/or a high value of the resistance of the amorphous regions. If, moreover, a phase transition takes place in the crossover temperature range, it would certainly affect the geometrical factors of the domains contributing to the measured conductance and lead to more complex conductance – temperature dependencies than those resulting from equations (1) and (2).

CONCLUSIONS

The conductivity of polyaniline – aqueous hydrochloric acid, $PANI_{ox}(0.42)$-HCl_{aq}, sample exhibits the temperature characteristics that indicate the heterogeneous structure of the electrodeposited polymer, in which a coexistence of the metallic and semiconducting regions occurs. To our knowledge, the crossover in the conductivity – temperature dependence of the thin film electrodeposited polyaniline was not reported earlier. The observed change in the electrical properties of the electrode material, occurring at ambient temperature, can be the origin of the changes in the electrode capacitance derived from the analysis of electrochemical impedance spectroscopy measurements shown in [2]. Nevertheless, an influence of the content of water on details of the conductivity – temperature dependence of the samples cannot be ruled off.

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