TEMPERATURE DEPENDENCE OF THE CONDUCTIVITY OF POLYANILINE SAMPLES

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ABSTRACT

The experimental system used to measure the temperature dependence of the conductivity of polyaniline samples (PANI) in this paper was based on a method of measuring changes in the polarity of the current which flows through a thin sample, in order to eliminate the adverse effects of parasitic voltage on the measurement results. Based on the measured resistance values we calculated conductivity of the treated plyaniline sample and demonstrated its temperature dependence. All measurements were perfomed an a vacuum.

Key words: polymers, polyaniline, activation energy, jump temperature, conductivity.

1. INTRODUCTION

In the very beginning of the study of conductive polymers the main research objective was to understand the fundamental processes in them, whereas today the main goal of the research is their technological applications. This is particularly evident after the discovery of polymer LEDs (light emitting diodes) 1990 by Richard Friend's [1]. One of the most promising conductive polymers is polyaniline (PANI). In the undoped state it is an insulator. Polyaniline may be doped, i.e. in the production process itself or subsequently, atoms or ions of some other substances may be added. It has been shown that doping significantly affects the conductivity of polyaniline.

2. EXPERIMENTAL RESULTS

The experimental system used to measure the temperature dependence of conductivity of PANI samples in this study consisted of: a programmable current source, digital nanovoltmeter, devices to measure and control temperature, a closed-cycle refrigerator - CCR, a vacuum system and a PC computer with built-in GPIB card (General Purpose Interface Bus), (Figure 1). Measuring of the resistance of doped polyaniline samples is performed using direct current (DC method). During measurement, a constant current is passed through the sample. Its value ranged, depending on the measurement, from 10 nA up to 1μA. Computer executes reading and memorizing of the temperature resistance (T, R (T)). After each voltage reading at a given temperature the computer sends a signal to the power source to change the polarity of the current, and the voltage reading is again executed. From so measured voltages for the positive (+ I) and negative (-I) polarity of the current, is determined the average value of the voltage $V = (V_+ + V-)/2$, from which is then calculated the resistance of the sample. In this way, we reduce the influence of parasitic voltages, for example the influence of thermal voltage. All measurements were performed in a vacuum. Based on the measured resistance values is calculated conductivity of the treated polyaniline sample.

Current-voltage characteristic of PANI-HCl doped polyaniline at room temperature is given in Figure 2. The figure shows linear i.e. Ohm's behavior. By linearization, using the least squares method, is obtained functional dependence of voltage on the current. From the slope of that dependence is obtained the resistance of the sample between the voltage contacts, which by knowing the size of the sample gives its conductivity. From the current - voltage characteristics of polyaniline samples it can be seen that all the samples have ohmic voltage dependence of the current intensity at room temperature (Figure 2).

Figure 1. Measuring system used to determine the conductivity

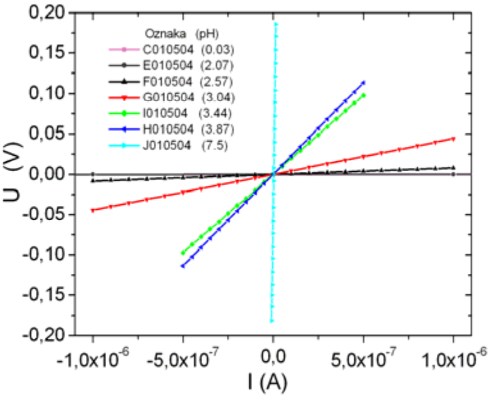


Figure 2. Current-voltage characteristics of polyaniline samples

Polyaniline samples that were used for experimental research in this paper were obtained by direct oxidation of aniline, using the Ammonium Peroxydisulfate $(NH_4)_2S_2O_4$ as oxidizing agent [2]. Doping was made by solution of hydrochloric acid (HCl) with different concentrations. Then we accurately measured dimensions of the samples (length, width, height) whose values are presented in Table 1. On the basis of Mott's quasi-one-dimensional VRH model by the relation $T^*=tg^2\beta$ were experimentally calculated hopping temperatures and activation energies whose values are also presented in Table 1. Activation energies were calculated by multiplying the hopping temperature by the Boltzmann constant. The parameter T * is determined by the highest barrier that appears in the polymer chain and is called the temperature of hopping. It depends on the density of states at the Fermi level $N(E_F)$ and the localization length. Then were measured resistance values of samples at room temperature and on that basis was calculated conductivity for each sample

Table 1. Specific parameters of conductivity

Dimensions of sample (L-W-H) (mm)	pH value of HCl solution	Hopping temperature T^* (K)	Activation energy (eV)	Resistance at room temperature (Ω)	Conductivity at room temperature (S/m)
4,5-5,1-0,9	0,03	7010	0,60	5,6	167
5,1-5,1-0,8	2,04	12696	1,09	23,7	53
4,9-5,1-0,7	2,59	19572	1,69	8180,0	0,175
3,9-5,1-1,0	3,87	49684	4,29	227044,0	0,003

Parameters which affect the conductivity of polyaniline are shown in the following charts:

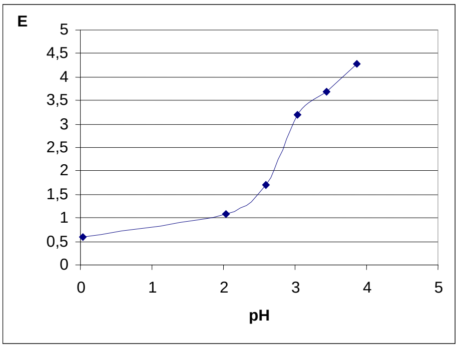


Figure 3. The dependence of the activation energy on pH values

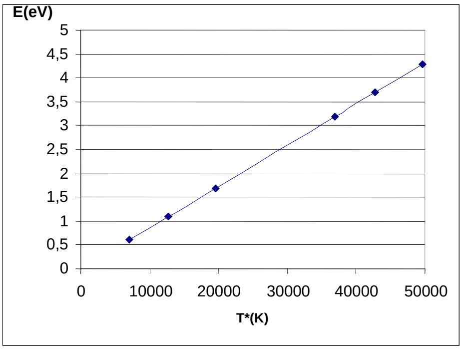


Figure 4. The dependence of the activation energy on the hopping temperature

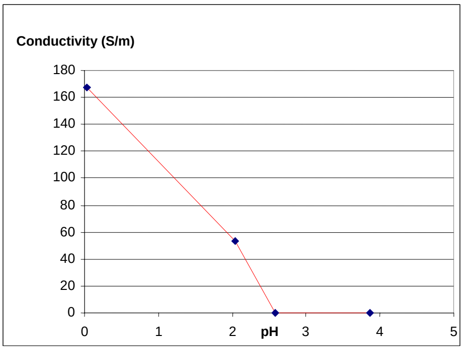


Figure 5. The dependence of the conductivity on pH values

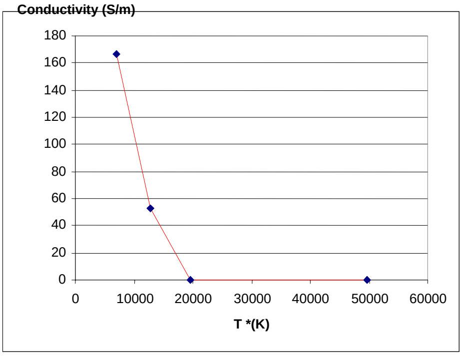
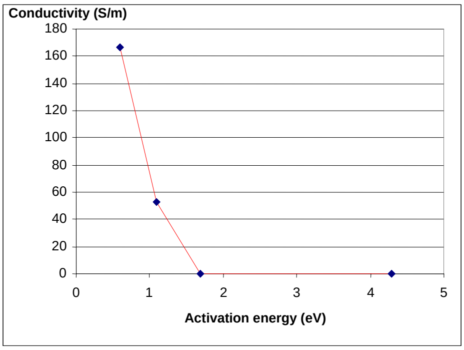


Figure 6. The dependence of the conductivity on the hopping temperature



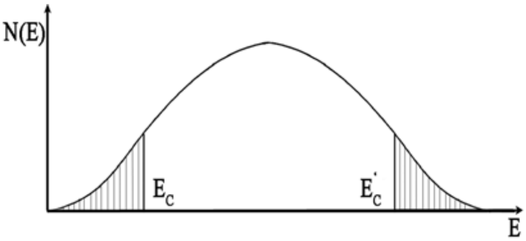


Figure 8. Density of states in disordered systems

Figure 7. The dependence of the conductivity on activation energy.

These results are consistent with Mott's model of the variable range hopping mechanism (Variable Range Hopping - VRH) [3]. Under this model, if the Fermi level lies above the mobility treshold E_μ conductivity is described by the Arrhenius's law of conductivity [4]:

$$\sigma(T) = C\exp\left(\frac{-(E_\mu - E_F)}{k_B T}\right)$$

If the Fermi level is below the mobility threshold then the states at the Fermi level are localized and electrons can not move freely but only by phonon-assisted hoping between localized states. According to N.Mott this mechanism of conductivity should exist only at low temperatures [3]. The connection between the hopping temperature T * and density of states at the Fermi level $N(E_F)$ is given by the relation:

$$T^* \propto \frac{1}{N(E_F)}$$

From the previous relation it is seen that if the hopping temperature is smaller then the density of states at the Fermi level is higher and thus the conductivity of sample is better, which is consistent with the experimentally obtained dependence of the conductivity on the hopping temperature (Figure 6).

Experimental results are also in line with the Mott-Davies model of density of states in disordered systems, which is shown in Figure 8. The band of this system is expanded in relation to a band of ordered crystals. In the "tails" of the band, that is for the energy less than E_C and greater than E'_C there are localized states. Between the energies E_C and E'_C states are extended, and by increasing the degree of disorder the area of extended states is getting narrowed. If the Fermi energy lies in an area of localized states such a system is called the "Fermi glass." Its conductivity at T = 0 K disappears, while at $T \neq 0$ K conductivity is possible only by thermally activated hopping between localized states. When the Fermi energy exceeds the "threshold of mobility" ($E_F > E_C$) the system will go into metallic state with finite conductivity [5].

Based on the previous it can be concluded that the activation energies for the experimentally obtained samples are found in "tails" of the band (parts with vertical lines pattern), because our samples do not have metallic conductivity. The activation energies for our experimentally obtained samples are in the range from 0,60 to 4,29eV, which corresponds to the activation energies for semiconductors. If those energies are lower, then also lower are prohibited energies E_g and so the electricity carriers will sooner hop from the valent into the conductve band. Thus, lower activation energies correspond to better conductivity, which is consistent with experimentally obtained results (Figure 7).

3. CONCLUSION

Based on the experimental results obtained we can make the following conclusions:

- Activation energies are higher if the pH value is higher, ie, when there is less doping
- The dependence of the activation energy from the temperature hops is linear,
- Dependences of conductivity on pH values, the hopping temperature and the activation energy are very similar in the character, that is there firstly occurs a slight increase in conductivity, and then there is a sudden hopping increase in conductivity,
- If the hopping temperature is lower then the density of states at the Fermi level is higher, and thus the conductivity of the sample is better which is consistent with the experimentally obtained dependence of conductivity on the hopping temperature
- Experimental results obtained are consistent with Mott's theory of conduction with the mechanism of variable range hopping (Variable Range Hopping - VRH) and the Mott-Davies model of the density of states.

4. REFERENCES

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