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ELECTRICAL CONDUCTIVITY OF SYNTHETIZED AND CONTROLLABLY DOPED POLYANILINE AT LOW TEMPERATURES

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ABSTRACT
This paper refers to a polyaniline produced by the direct oxidizing method at 0ºC. There were performed two controlled dopings of polyaniline with hydrochloric acid (HCl). Resistance of the samples was measured within the temperature interval from 10 K to 290 K, in the process of cooling and heating. The conductivity exponent 1/2 was calculated from the functional dependency of the sample resistance from the temperature. After the second deprotonation carried out, with two various concentrations of ammonium water solution (0,2M and 2M), and the repeated controllable doping with HCl, it was shown that there occurs a change in the resistance dependency of all samples in this series, and in this case the exponent of electrical conductivity has the value of 2/5 which corresponds to the 3d mechanism of electricity conduction. These results are in accordance with the Fogler, Teber and Shklovskii theory, published in 2004, and represent the first experimental confirmation of the above mentioned theory.
Keywords: polymers, polyaniline, production, doping, conductivity, electrical properties.

1. INTRODUCTION

Polyaniline belongs to the new group of synthetic materials. Its simplicity and low price synthesis procedure, stability of final product, combination of typical properties and easily controlled electrical conductivity makes this material interesting for wide range of applications – from anticorrosive protection to plastic microelectronics. Conductive polymers are materials which have excellent characteristics for application in various industrial branches. Conductivity of polymers was firstly achieved in 1977 [1], and it became interesting for research in 1980-ies. Polyaniline is one of the materials which was researched more than any other material from this group. The first attempts to describe the nature and mechanism of conductivity in polymers were based on the assumption that polymers were similar to amorphous semiconductors. Although the pursuit for an adequate theory of polymer conductivity has lasted several decades already, still there is no established clear model of conductivity [2].

2. EXPERIMENTAL RESULTS

The samples of polyaniline which were used for experimental researches in this paper were obtained by direct oxsidation of aniline, with usage of ammonium peroxide sulphate $(NH_4)_2S_2O_4$ as the oxidizing agent [3]. The first doping was made by solution of hydrochloric acid (HCl) in various concentrations. Afterwards, there were performed measurements of electrical resistance in the temperature interval from 10K to 290K, and it was shown that their resistance has the following dependency $\ln R = CT^{-1/2}$. The stated results are in accordance with the Mott's one-dimensional VRH (Variable Range hopping) model [4].

After measurements were taken, repeated deprotonation of samples was performed but with different concentration of Ammonium water solution. Two deprotonations were performed:

- deprotonation A with 2M concentration of Ammonium water solution
- deprotonation B with 0,2M concentration of Ammonium water solution

Doping is performed again with water solution of HCl. Measured acidness of doped samples was :

- for deprotonation A pH=0,02; pH=1,49; pH=1,91; pH=2,43;
- for deprotonation B pH=1,91 and pH=2,3.

We tried, for these samples, to graphically present the dependence of logarithmic change of standard resistance on T $^{-1/2}$. The results showed that there was no linear dependence, which means that for those samples the Mott's theory of conductance does not apply. To find linear dependence for these samples we should determine α coefficient beforehand:

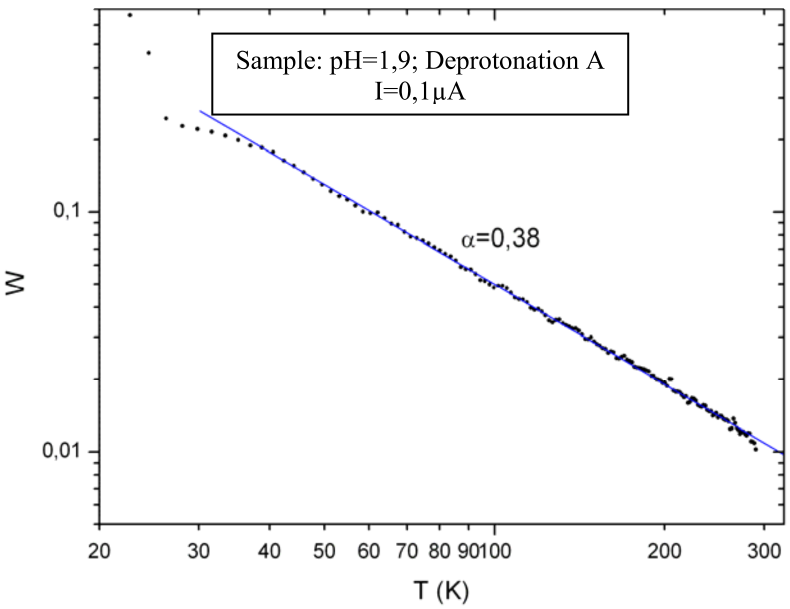

Figure 1. Dependence of excerpt $-\frac{d}{dT}\ln\frac{R}{R_{290}} = W$ *on temperature for sample pH=1,91*

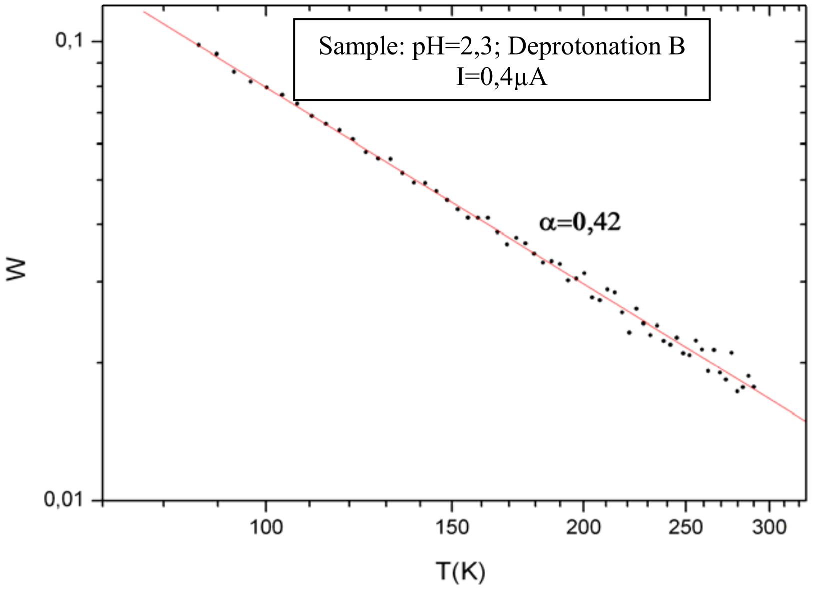

Figure 2. Dependence of excerpt W on temperature T for sample pH=2,3

For previous graphics, coefficient α was calculated in the following way:

Dependence of resistance transformation is : $R = R_0 e^{\left(\frac{T_0}{T}\right)^{\alpha}}$

$$R_{290} = R_0 e^{\left(\frac{T_0}{T_{290}}\right)^{\alpha}} \quad \Rightarrow \quad R_0 = R_{290} e^{-\left(\frac{T_0}{T_{290}}\right)}$$

$R = R_{290} e^{-\left(\frac{T_0}{T_{290}}\right)^{\alpha}} e^{\left(\frac{T_0}{T}\right)^{\alpha}}$ taking the logarithm we get: $\ln \frac{R}{R_{290}} = -\left(\frac{T_0}{T_{290}}\right)^{\alpha} + \left(\frac{T_0}{T}\right)^{\alpha}$ first excerpt by temperature is:

$\frac{d}{dT} \ln \frac{R}{R_{290}} = T_0(-\alpha) T^{-(\alpha+1)}$ if we bring in the designation: $\frac{d}{dT} \ln \frac{R}{R_{290}} =$-W

and multiply the previous equation with (-1), follows:

W=$\alpha T_0^{\ \alpha} T^{-(\alpha+1)}$ take the logarithm of this equation:

$$\log W \propto -(\alpha+1)\log T \quad \Rightarrow \quad \alpha = 1 - \frac{\log W}{\log T} = 1 - tg\beta$$

Middle value of experimentally determined exponent is:

$$\overline{\alpha} = 0{,}40 = \frac{2}{5}$$

which is in accordance with Folger-Teber-Shklovskii theory, who calculated the same value theoretically, for 3d chain-like conductors, and which includes Coulomb electron-electron interaction [5].

Dependence of standard resistance after the second deprotonation on T $^{-2/5}$, for all samples, is shown on the following figure:

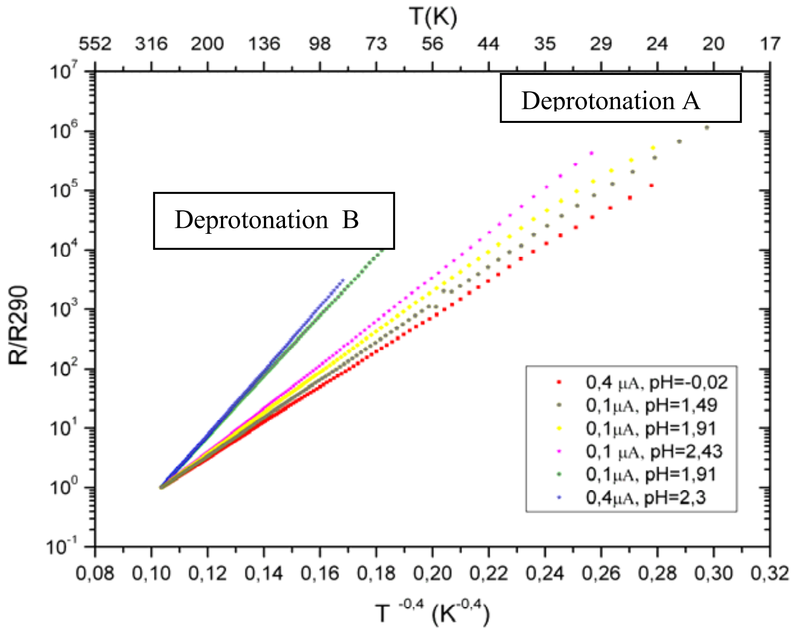

Figure 3. Temperature dependence of standard resistance after second deprotonation and second doping

3. CONCLUSION

In the temperature range from 290 K to 150 K the resistance of all samples, for the first doping, has the dependency $\ln R = CT^{-1/2}$, from which we can see that in this temperature range there can exist the quasi-one-dimensional (Q1D) conduction mechanism. The exponent 1/2 corresponds to Mott's VRH theory of conductivity, without Coulomb's electron-electron interaction [4]. After the second deprotonation with two various concentrations of ammonium water solution (0,2M i 2M), and repeated doping with HCl water solution, we obtained the resistance dependency for all samples in this series as $\ln R = CT^{-2/5}$, which corresponds to the Q3d VRH conduction mechanism for electrical current. Experimentally determined exponents for conductivity of doped polyaniline (1/2 and 2/5) are in accordance with the Fogler, Teber and Shklovskii theory, published in 2004. These results represent the first experimental confirmation of this theory. We can conclude that Coulomb's interaction changes the exponent and that the physical meaning of the exponent is – the measure of Coulomb's interaction of electrons.

4. REFERENCES

[1] C.K.Chiang, C.R. Fincher, Y.W.Park, A.J.Heeger, H.Shirakawa, E.J. Luis, S.C.Gau i A.J. MacDiarmid, *Phys.Rev.Lett.*, 39, 1098 (1977)
[2] A.J.Heeger, Semiconducting and metallic polymers: The fourth generation of polymeric materials, Nobel Lecture, December 8 (2000)
[3] I. Gazdić, H. Smailhodžić, D. Babić, B. Leontić, I. Kokanović, Z. Micković, M. Novak, M. Baćani, *Postupci i metode dobivanja vodljivog polimera polianilina,* Zbornik radova Prirodno-matematičkog fakulteta br.1, 211, Tuzla, 2004.
[4] Izet Gazdić, Dinko Babić, *Applications of Mott's theori of conductivity on doped polyaniline,* 10th international research/expert conference, TMT-2006, pp. 1235, Barcelona – Lloret de Mar, 2006.
[5] M. M. Fogler, S. Teber and B. I. Shklovski, Variable-range hopping in quasi-one-dimensional electron crystals, *Phys. Rev.*B.69 (2004)