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Fig. 1

Figure 1: Fig. 1

## Abstract

## Full Text

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# ON THE MECHANISM OF CONDUCTIVITY IN ORGANIC SEMICONDUCTING POLYMERS

*(Presented by Academician V. A. Kargin on 27 IX 1962)*

Earlier ([1]), in order to elucidate the mechanism of electrical conductivity in thermally treated polyacrylonitrile (PAN), the temperature dependences of the resistance and of the thermo-e.m.f. were investigated; the measurements were carried out in air on specimens differing both in the temperature and in the medium of the thermal transformation. The specimens studied were either pressed pellets or fabrics. As a result of the investigations it was concluded that the temperature dependence of the resistance is determined by the exponential temperature dependence of the mobility at an unchanged concentration of current carriers. In this case, as for all polymers studied up to now, the sign of the current carriers in thermally treated polyacrylonitrile, determined from the sign of the thermo-e.m.f., was positive. Later, a strong influence of adsorbed gases on the magnitudes of the electrical conductivity and of the activation energy of the electrical conductivity of thermally treated PAN was established, manifesting itself in a decrease in the resistance and in the activation energy of the conductivity of the specimens when they were heated in vacuum.

In the present work, a systematic investigation was undertaken in a vacuum of $5 \cdot 10^{-6}$ mm Hg of the temperature dependences of the resistance and of the thermo-e.m.f. on specimens made from fibers of thermally treated polyacrylonitrile, differing only in the temperature of the thermal transformation.

In Figs. 1 and 2 are given characteristic temperature dependences of the resistance and of the thermo-e.m.f. for some PAN specimens differing in treatment temperature. Table 1 presents the values of the specific resistances and thermo-e.m.f. relative to lead, taken at 100°, for all investigated specimens with treatment temperatures from 520 to 730°, measur–

**Fig. 1.** Dependence of the specific resistance on temperature for PAN speci-

Fig. 2. Dependence of the differential thermo-e.m.f. on temperature for PAN samples with treatment temperatures: 1—640, 2—670, 3—700°. a—first heating, —cooling, —second heating

Figure 2: Fig. 2. Dependence of the differential thermo-e.m.f. on temperature for PAN samples with treatment temperatures: 1—640, 2—670, 3—700°. a—first heating, —cooling, —second heating

Figure 3 and Figure 4

Figure 3: Figure 3 and Figure 4

mens with treatment temperatures: 1 —580, 2 —40, 3 —700°; *a* —first heating, *b* —cooling, *c* —second heating.

···before and after heating the samples in vacuum. As can be seen from the figures and from the data of Table 1, during the first heating of the samples in vacuum to 420° the resistance and the thermo-e.m.f. change irreversibly; moreover, as a result of heating, the resistance decreases by approximately a factor of 3 for the sample with a treatment temperature of 730° and by a factor of 10 for the sample with a treatment temperature of 520°.

**Fig. 2.** Dependence of the differential thermo-e.m.f. on temperature for PAN samples with treatment temperatures: 1—640, 2—670, 3—700°. *a*—first heating, —cooling, —second heating.

Even greater is the effect of heating in vacuum on the thermo-e.m.f. For all samples, except the sample with a treatment temperature of 730°, the thermo-e.m.f. changes sign, i.e., the samples which in air had hole conductivity become electronic after heating in vacuum. During repeated heating of the samples in vacuum to 420° the resistance and the thermo-e.m.f. change reversibly. The decrease in the resistance of heat-treated PAN and the change in the sign of the current carriers from positive to negative (according to the sign of the thermo-e.m.f.) as a result of heating in vacuum we explain by desorption of gases. This is confirmed by the fact that, when the degassed samples are brought out into air, their resistance restores its initial value, and the thermo-e.m.f. again becomes positive.

Figure 3 presents the temperature dependences of the thermoelectric power of samples preliminarily heated in a vacuum of $5 \cdot 10^{-6}$ mm Hg for several hours at the maximum temperature (420—440°), i.e., degassed to such an extent that their temperature dependences of resistance and thermoelectric power became completely reversible. It is seen from this figure that

**Fig. 3.** Dependence of the differential thermoelectric power on temperature for PAN samples with treatment temperatures:
1—520, 2—580, 3—600, 4—620, 5—640, 6—670, 7—680, 8—730°, preliminarily degassed by heating in vacuum.

*a*—cooling, *b*—heating

**Fig. 4.** Dependence of the thermoelectric power on the logarithm of the electrical conductivity for heat-treated PAN.
1—experimental, 2—theoretical

the thermoelectric power of samples with low treatment temperatures (520, 580, and 600°) increases linearly with increasing temperature. Samples with a high treatment temperature (670, 680, 700, and 710°) have, at room temperature, a small negative value of thermoelectric power, which decreases to zero as the measurement temperature is raised, and with further increase in temperature the thermoelectric power becomes positive and then increases somewhat. For these samples, Table 1 gives the temperature at which the thermoelectric power changes sign to zero. The temperature dependence of the thermoelectric power for degassed samples, as it seems to us, indicates that in the substances under study the current carriers are in a state of either complete or partial degeneracy; their concentration does not depend on temperature, and consequently the exponential decrease in resistance with increasing temperature, as also for porous samples in measurements in air, is determined by the exponential growth of the effective mobility of the current carriers [(2)].

The assumption of degeneracy of the current carriers in the samples studied is also confirmed by the form of the dependence of the thermoelectric power on electrical conductivity, corresponding to a temperature of 100°, for all the samples investigated (see Fig. 4). For comparison, Fig. 4 presents a theoretical curve of the dependence of thermoelectric power on electrical conductivity, constructed on

on the basis of the most general expression for the thermoe.m.f. as a function of concentration at any concentration of current carriers of one sign, taking into account the following assumptions: (a) the effective mobility of the current carriers does not change with increasing treatment temperature and is the same for all samples; (b) the mean free path of the carriers does not depend on energy.

**Table 1**

| Treatment temp., °C | $\rho_1$, ohm · cm | $\rho_2$, ohm · cm | $\alpha_1$, $\mu$V/°C | $\alpha_2$, $\mu$V/°C | Temp. at which $\alpha = 0$, °C |
|---|---|---|---|---|---|
| 520 | $4.6 \cdot 10^3$ | $4.6 \cdot 10^2$ | – | −104 | – |
| 580 | $2.9 \cdot 10^2$ | 25 | – | −42 | – |
| 600 | $3.3 \cdot 10^2$ | 46 | – | −48 | – |
| 620 | 40 | 5.5 | – | −22 | – |
| 640 | 18 | 3.8 | – | −17 | – |
| 640 | 17 | 2.9 | +88 | −15 | – |
| 670 | 4.2 | 1.5 | +61 | −8.8 | 425 |
| 680 | 1.8 | 0.5 | +54 | −4.8 | 410 |
| 700 | 1.4 | 0.48 | +45 | −2 | 235 |

| Treatment temp., °C | $\rho_1$, ohm · cm | $\rho_2$, ohm · cm | $\alpha_1$, $\mu$V/°C | $\alpha_2$, $\mu$V/°C | Temp. at which $\alpha = 0$, °C |
|---|---|---|---|---|---|
| 710 | 0.37 | 0.15 | +36 | −0.4 | 120 |
| 730 | 0.42 | 0.15 | +26 | +0.7 | – |

**Note.** $\rho_1$ and $\alpha_1$ are the values of the specific resistance and thermoe.m.f., respectively, measured before heating the sample in vacuum. $\rho_2$ and $\alpha_2$ are the corresponding values measured after heating the samples in vacuum.

One point on the theoretical and experimental curves has been made coincident; this corresponds to a mobility equal to $1.3 \cdot 10^{-3}$ cm$^2$/V · sec, if the effective mass of the carriers is taken equal to the mass of a free electron. As can be seen from the figure, the theoretical curve is steeper than the experimental one. This apparently indicates that the mobility of different samples is different and increases with increasing treatment temperature.

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*Note: Figure translations are in progress. See original paper for figures.*