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Abstract

Full Text

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Electrical Properties of Systems Consisting of Tetracyanoethylene and Powdered Metals

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The study of compositions of highly dispersed metals and organic polymers ([1], [2]) showed that these systems possess certain electrophysical properties characteristic of semiconductors. By varying the methods of obtaining these compositions, it was possible to influence their properties. Most of the systems studied were prepared from highly dispersed iron and a number of organic polymers ([1], [2]), which did not contain any structural elements capable of facilitating the passage of electrons.

It seemed of interest to study the properties of such compositions that consist of dispersed metals and organic polymers possessing semiconducting properties. Tetracyanoethylene (TCNE) was chosen as such an object; as had been shown earlier ([3]), at elevated temperatures it reacts with metals with the formation of polymeric chelate compounds. The physical properties of TCNE made it possible to apply a new method for obtaining the metal–polymer system, namely, treatment of powdered metals with vapors.

Fig. 1. Apparatus for obtaining compositions from tetracyanoethylene and powdered metals

A. A. Berlin, L. I. Boguslavskii, et al. ([4]) observed that, upon interaction of TCNE vapors with the surface of iron, as well as copper plates, thin films of chelate polymers are formed (of the order of 10^{-6} cm), possessing conductivity of the semiconductor type and a number of other interesting electrophysical properties.

Figure 1 shows the apparatus in which compositions from dispersed metals and TCNE were prepared. Dispersed iron was introduced into part *A* of the apparatus (usually 0.3 g); TCNE powder (0.1 g) into part . The apparatus

was sealed to a high-vacuum installation. After a vacuum had been established, the apparatus was sealed off (B) and fixed in a special holder (Γ) connected to the motor shaft. The apparatus with the holder was placed in a furnace; heating of the system took place with continuous rotation of the apparatus. The construction and arrangement of the experiment described made it possible to treat the surface of the dispersed metal with TCNE vapors over a wide temperature range. Owing to rotation of the apparatus, continuous pouring of the powdered metal was ensured, which promoted the formation on its surface of a uniform film of the TCNE polymer complex. After completion of the process and cooling to room temperature, the ampoule was opened and the resulting product was removed from it; the latter was pressed under a pressure of about 6000 kg/cm^2 into rectangular plates, on which various physical properties of the compositions could be studied.

Determination of the electrical conductivity of these specimens as a function of temperature was carried out in vacuum and, as in our previous experiments, stable results were obtained only after prolonged heating at 200–250° ([1], [2]). A series of experiments was carried out in which the reaction yield—

the compositions was carried out at 250°, with the duration of this process being varied. Figure 2 shows the curves of the dependence of the logarithm of the electrical conductivity ($\lg \sigma$) on temperature ($10^3/T$) in the range from +160° to −80° for three samples.

As can be seen from Fig. 2, the dependence $\lg \sigma(1/T)$ is linear in character, and the magnitude of the electrical conductivity increases with increasing temperature.

Table 1

System: powdered iron + TCNE

Sample No.	Amount of substance, g: iron	Amount of substance, g: TCNE	Duration of reaction for preparing the composition, h	Temp., °C	Specific electrical resistivity at 20°, ohm · cm	Activation energy of conductivity, eV	Thermo-emf magnitude, μV/deg	Type of conductivity according to thermo-emf data
1	0.3	0.1	2	250	$4.5 \cdot 10^{-2}$	0.03	6	p
2	0.3	0.1	14	250	$1.4 \cdot 10^{-1}$	0.04	9	p

Sample No.	Amount of substance, g: iron	Amount of substance, g: TCNE	Duration of reaction for preparing the composition, h	Temp., °C	Specific electrical resistivity at 20°, ohm · cm	Activation energy of conductivity, eV	Thermo-emf magnitude, μV/deg	Type of conductivity according to thermo-emf data
3	0.3	0.1	20	250	$8.6 \cdot 10^3$	0.24	–	n
4	0.3	0.1	2	250	2.65	0.05	–	p
5	0.3	0.1	15	250	$2.9 \cdot 10^3$	0.1	–	n
6	0.6	0.05	20	250	$2.0 \cdot 10^{-1}$	0.04	–	
7	0.6	0.05	20	350	7.4		9	n

Table 1 gives the results of measurements of various electrophysical properties of these compositions, as well as the values of the activation energy ΔE of conductivity. From these data it follows that the duration of the reaction has a substantial effect on the properties of the composition. With increasing reaction time, the resistance of the sample and the activation energy of conductivity increase sharply (Nos. 1, 2, 3). Thus, the resistance changed by almost 5 orders of magnitude, and the activation energy from 0.03 eV to 0.24 eV. The type of conductivity, which in samples Nos. 1 and 2 was the same as in p-semiconductors, after heating for 20 h, as seen for sample No. 3, becomes the same as in n-semiconductors.* In other series of experiments (for example, Nos. 4, 5) quantitative reproduction of the results was not achieved. However, the direction of change in the properties of the samples was preserved. Apparently, it has not yet been possible to take into account precisely all the factors affecting the course of the reaction.

In the works of Epstein and Wildi [(5)], devoted to polyphthalocyanines, both p- and n-conductivity were likewise observed. In these authors' work, n-conductivity usually changed into p-conductivity after prolonged heating in vacuum, which was probably accompanied by removal of foreign impurities. In the case described by us, a different phenomenon is taking place, since samples with both p- and n-conductivity were subjected to prolonged heating in vacuum and nevertheless retained the sign of conductivity.

Fig. 2. Dependence of the logarithm of electrical conductivity ($\lg \sigma$) on temperature ($10^3/T$) for the iron–tetracyanoethylene system. Duration of the reaction

Fig. 2

Figure 2: Fig. 2

Fig. 3. Dependence of the logarithm of the electrical conductivity $\lg \sigma$ on temperature for the silver–tetracyanoethylene system

Figure 3: Fig. 3. Dependence of the logarithm of the electrical conductivity $\lg \sigma$ on temperature for the silver–tetracyanoethylene system

for preparing the sample: 1 –2 h, 2 –14 h, 3 –20 h.

* As we previously showed for the iron–polyisoprene system, and also for iron–polyisobutylene [1,2], the transition from p-conductivity to the n-type is associated with thermal treatment of the samples, which may cause both a change in the character of the bond between the polymer and iron and a rearrangement of the polymer, or even its partial destruction.

Microchemical analysis of the TCE films formed on the surface of iron in experiments Nos. 2 and 3 indicates that, despite the sharp difference in the properties of these samples, the carbon content in them is the same.

Determination of the surface area of the powdered iron was carried out by the method of low-temperature nitrogen adsorption (BET), and for our sample it was 2 m^2/g. The carbon content, according to the analysis, was 2% of the weight of the iron. If one assumes a planar azaporphyrin structure of the polymeric components of TCE with metals, then two TCE molecules correspond to one iron atom. The calculation shows that the surface of the iron is covered by 3-4 molecular layers of the polymeric complex.

Fig. 3. Dependence of the logarithm of the electrical conductivity $\lg \sigma$ on temperature for the silver–tetracyanoethylene system

If the data for samples Nos. 3, 4, and 5 are compared with 6 and 7, it is seen that a decrease in the amount of TCE in the reaction sharply lowers the specific resistance of the composition. During storage of iron–TCE samples in air, strong corrosion is observed. This phenomenon should be specially studied.

In addition to iron, a composition of TCE with silver was also investigated. Figure 3 shows that in this composition the temperature dependence of the electrical conductivity is also of the semiconductor type. The reaction conditions for obtaining the composition are the same as for sample No. 3 (Table 1), i.e., heating at 250° for 20 h. The specific resistance at 20° is $1.2 \cdot 10^4$ ohm $\cdot$ cm; the activation energy and the t.e.m.f. are of the same order as for sample No. 3.

In estimating the thickness of the film on the basis of the true surface area of the silver and the results of microchemical analysis, the film of the polymeric chelate complex of TCE, as in the case of iron, consists of 3-4 molecular layers. Experiments with silver also indicate that the temperature regime of the reaction

plays a very substantial role in creating the properties of compositions made from polymers and dispersed metals.

There are still far from enough experimental data with TCE to draw any final conclusions. However, the results obtained allow one to conclude that, by changing the reaction conditions, it is possible to vary over a wide range the electrophysical properties of these compositions.

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