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On the possibilities of the use of phthalocyanines in photovoltaic conversion

M. ZĄBKOWSKA-WACŁAWEK*, Z. ZIEMBIK
University of Opole, ul.Oleska 48, 45–052 Opole, Poland
E-mail: Maria.Waclawek@uni.Opole.pl

The electrical properties of semiconductor and semimetal composites (containing CuPc and different carbon blacks) were described. Their properties may be varied in a wide range, dependently on carbon black type and preparation conditions. We expect that the photovoltaic properties of the materials can be applied for photovoltaic conversion and we discuss possibility of their practical utilisation.

1. Introduction

Recently, organic materials have attracted a great deal of interest due to their photoelectrical properties. It was found that a group of organic compounds could be used for photovoltaic cells construction [1, 2].

One of most investigated materials are phthalocyanines, macroheterocyclic compounds with structure similar to porphyrines. These materials show very good thermal stability and their transport properties could be modified and improved by doping process or mixing with other components.

The photoelectrical properties of systems comprising phthalocyanine and different forms of carbon were described by many authors. Among others utilisation of CuPc [3–6] and ZnPc [7–10], as electron donors in photovoltaic cells were described. As the electron accepting material C_{60} fullerene was usually taken into account. It was found that in some composite materials carbon nanotubes increased the yield of photovoltaic process [11, 12]. The results obtained were very promising, however for practical utilisation a lot of problems to solve still remains.

In our laboratory electrical properties of semiconductor and semimetal composites (containing CuPc and different carbon blacks) have been studied for years. Their properties may be varied in a wide range, dependently on carbon black type and preparation conditions. We expect that the photovoltaic properties of the materials can be applied for photovoltaic conversion and we discuss possibility of their practical utilization.

2. Investigated materials properties

In composite materials investigated copper phthalocyanine (*Cupc*) was low conducting component and carbon black (*cb*) was high conducting one. Copper phthalocyanine used in our experiments was a deep blue powder containing α form (determined by Stoe Powder Diffractometer) crystallites. The crystallite sizes investigated by Laser Granulation Analyser showed that the diameters distribution has 2 peaks at 10 and 50 μm.

Carbon black particles are small spheroidally shaped paracrystalline unit. Interconnected particles form aggregates—discrete, colloidal entities that are the smallest dispersible units of this material. Carbon black agglomerate is comprised of a large number of aggregates physically held together.

Carbon black is characterised by particle diameters and the surface properties, which can be determined, among others, by nitrogen and dibuthyl phthalate absorption (DBPA). Carbon black particle sizes are usually limited in the range approx. from 10 to 500 nm.

Two kinds of methods of the composite preparation were utilised. First of them involved homogenisation of the mixture by grinding the known amounts of *cb* and *Cupc* in the agalite mortar. To avoid mechanical stress during the homogenisation other method of preparation was utilised. Vesselus containing liquid suspension of Black Pearl 700 and *Cupc* in acetone were placed in the ultrasound bath for 20 min. Neither *Cupc* nor the carbon black was soluble in acetone. No significant influence of homogenisation time (within 10–60 min.) on the electrical properties of the mixture was observed. The material obtained was dried by heating in150°C for 5 h and kept in vacuum (approx. 0.1 Pa) for two days. Portions (0.25 g) of the materials obtained were compressed to obtain pellets of 10 mm in diameter and 2 mm thick. Our composites had small thermal conductivities and their electrical conductivity was changed from 10^{-7} to 10^{2} S/m.

The composite conductivity (σ) dependence on the volume fraction (f) of *cb*s content was quite well described by the McLachlan [13] and Yoshida [14] models as well as the equations derived from the percolation theory. Several relationships between the physico-chemical properties of *cb*s and the parameters from the models were found [15].

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*Author to whom all correspondence should be addressed.

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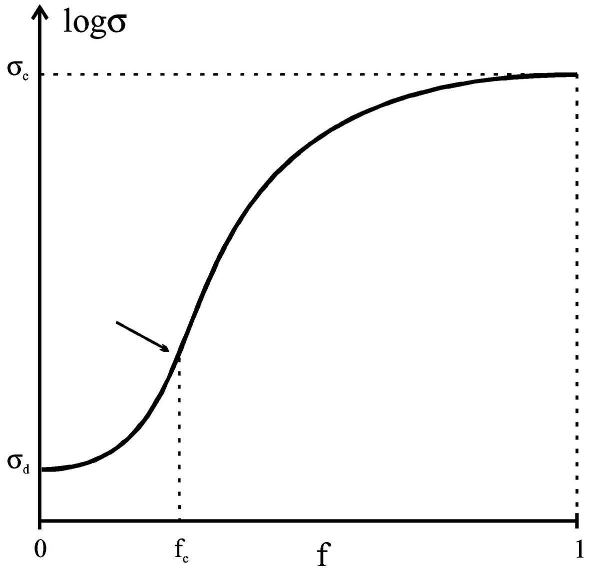

Figure 1 Typical plot of log(σ) vs. f dependence. The σ_c and σ_d were conductor and dielectric conductivities, respectively.

The figures in our work show scheme of changes observed for the materials investigated and do not concern particular sample. Typical plot of log(σ) vs. f is shown in Fig. 1. The σ_c and σ_d denotes conductor and dielectric conductivities, respectively. The arrow indicate the inflection point of log(σ) vs. f dependence for $f = f_c$. In the f range close to f_c electrical conductivity changes rapidly. Dielectric composite became conductor for $f > f_c$ or conductor became dielectric for $f < f_c$. This transition occurs when the cluster of conducting material connects or disconnects electrodes attached to composite sample. For *cb* containing composites f_c varied in the range from approx. 0.02 to 0.2. For a given *cb* fraction composite conductivity depended first of all on the carbon black type.

For most of the composites the σ dependence on temperature T investigations showed thermally activated mechanism of conduction described by the relationship:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \qquad (1)$$

where E_a – activation energy of conductivity, σ_0 – pre-exponential factor, k – Boltzmann constant.

It was found that for increasing f the E_a and σ_0 values decreased. For some certain composite compositions the log $\sigma(T^{-1})$ dependence showed E_a and σ_0 dependence on T. An example relationship plot was shown in Fig. 2.

Usually the E_a values ranges from 0.7 eV to approx. 0.01 eV. For $f \gg f_c$ appeared some deviation from log $\sigma(T^{-1})$ linearity supposing a change in conduction mechanism.

For some highly conductive composites a decrease in conductivity with increasing T was observed. This phenomenon is known as Positive Thermal Coefficient (PTC), occurring sometimes in composites comprised NTC (Negative Thermal Coefficient—conductivity of component increases with increasing T) components.

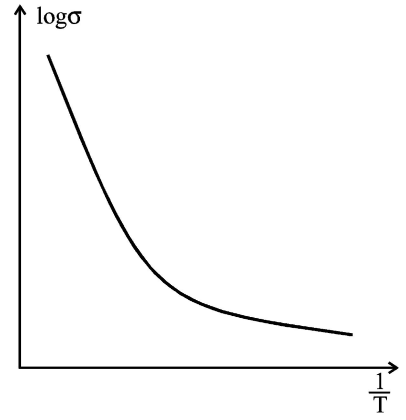

Figure 2 The log $\sigma(T^{-1})$ dependence where E_a and σ_0 were T dependent.

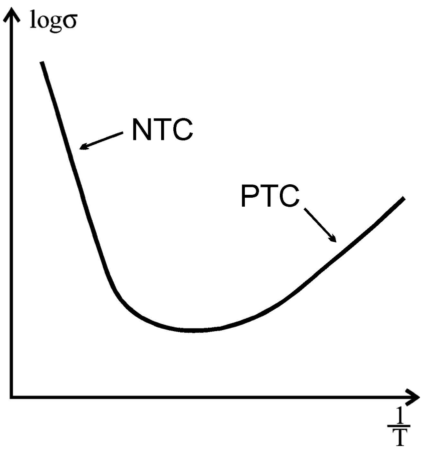

Figure 3 The log $\sigma(T^{-1})$ dependence where transition from PTC to NTC occured.

This phenomenon is usually explained assuming different thermal expansions of composite components. Higher thermal expansion coefficient of low conducting component than the high conducting one may result in destruction of conducting clusters connections. As the result PTC phenomenon might be observed. For some *cbs* and certain composite compositions the temperature depended transition from PTC to NTC was observed (Fig. 3).

3. Discussion

We expect that the described above properties might be useful for photovoltaic cell construction. In semiconductors the photons of energies lower than the energy gap between valence and conducting bands cannot create electron-hole pairs. Brown and Green have shown [16] that the photoconversion efficiency of properly doped semiconductor might theoretically reach 77.2%. High photovoltaic conversion efficiency is expected for the systems with a number of accessible electron states in the lower part of energy gap [16]. Appearance of electron band structures in *Cupc-cb* composites should not be taken into account because of their irregular structure. However, polycrystalline structure of *Cupc* and paracrystalline *cb* might produce a number of electronic states supporting charge carrier transfer to the states contributing electrical conductivity. For such electronic structure of material the long-wave photons should also be able to act in electron-hole pairs generation. After absorption of the high-energy photon the excess energy might be emitted as low-energy photons, which consecutively may take part in photovoltaic conversion.

Electric field in conductor-dielectric composite is distributed non-regularly. It may reach big values of tension in the gaps between conducting clusters. This composite region might act as traps on generated charge carriers. This would separate them, protecting against fast recombination. It could be expected that appearance of this region strongly depends on the *cb* type utilized in composite. Highly branched *cbs* should serve structures promoting appearance of narrow gaps between conducting carbon clusters.

Possibility of phthalocyaniens utilization as gas and vapor sensing material have been attracted a great deal of interest. Especially influence of oxidizing gases like O_2, NO_x or Cl_2 on electrical properties of thin phthalocyanine layers has been investigated [17–19]. It has been shown that these gases can change electronic structure of phthalocyanine surface. The influence of these changes on photovoltaic processes was also observed [4, 20]. Controlled chemical modification of surface might also provide a method of photoconversion enhancement.

4. Conclusions

In this paper we have supposed that phthalocyanine-carbon black composites might be utilized for photovoltaic cells construction. Their widely changeable but predictable electrical properties provide an advantage in design of solar cells and other devices using photoconvertion. To improve the photoelectrical conversion of phthalocyanine material its chemical modification should be also considered.

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