

SOME ELECTRICAL AND PHOTOELECTRICAL PROPERTIES OF PEPC AND 3,6-di-Br-PEPC BASED FILMS WITH V₂O₅ NANOPARTICLES

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The peculiarities of a charge flow in the “sandwich”-type ITO/composite/In structures based on polyepoxypropylcarbazole (PEPC) and 3,6-di-Br-PEPC polymer composite films with nanosized V₂O₅ have been studied. The increase of the V₂O₅ concentration in polymer was found to affect nonmonotonously the current-voltage characteristics (CVC), except the case of 3,6-di-Br-PEPC at the applied “+” bias. The maximum photosensitivity was demonstrated by the structures of PEPC with V₂O₅ minimum concentration (33.82 wt.%) and 3,6-di-Br-PEPC with a dopant maximum concentration (42.67 wt.%) at a negative potential applied to In. The differential slope of curves α is not definitely dependent on V₂O₅, polarity, or illumination; α is not constant varying by the voltage increase from 1 to 2.5 V for every special case. Some plots of CVC curves were found to have $\alpha=1.25$, which is, evidently, proper for polymers and non-ordered structures.

Introduction

The development of new organic conducting polymers (CP) having a system of conjugated bonds with useful physico-chemical, electrophysical, spectra, and other properties as well as broadening the spheres of their application is one of the topical and currently most intensively studied problems of to-day chemistry and molecular materials sciences [1, 2]. Among the characteristics of a special interest, CP’s inherent semiconducting properties should be mentioned first of all. Poly(N-vinylcarbazole) (PVC) and PEPC both doped and undoped should be ascribed to this type of CP. At present, these polymers found a wide application as media for information registration and optical recording media in electrography [3]. Work [4] has reported a feasibility to use the SbCl₅-doped CdTe/PEPC heterostructures as converters of light energy into electric one and light emission sensors in a wide spectral range. Upon PVC and PEPC doping with stibium pentachloride, the conduction of these polymers was found to rise due to the formation of conjugated bonds during the doping process [5]. Moreover, it

was recently reported [6] that, since polyaniline interacts with V₂O₅ and Fe₃O₄ soles, intercalation-type nanocomposites are formed, where polyaniline intercalates into V₂O₅ and Fe₃O₄ interlayer galleries. Owing to this, some physico-chemical characteristics of composites are essentially changed, thus attaining a new level of functional application for the polymeric materials with a system of conjugated bonds. CP are also promising materials for applications in electronics. They may be applied both as contacts and a layer in a multilayer system or a component in a multicomponent single-layer light-emitting “sandwich” structure. Works [7, 8] report a possibility to use PVC and its derivants as a functional layer of electroluminescent diodes, which opens one more potential field for PEPC applications.

There is still no clear understanding of the mechanisms of a charge flow, the injection of current carriers, and their recombination. It does not allow to control the above processes in order to rise the structure photosensitivity and the efficiency of conversion of electric energy into light energy when using these polymers.

In this work, the differential method [9–11] is used to investigate the peculiarities of a charge flow, the injection of current carriers from contacts as well as photoconduction in the structures based on poly(N-epoxycarbazole) and 3,6-di-poly(N-22epoxypropylcarbazole) with nanosized V₂O₅.

1. Experimental Procedure

The samples were prepared from PEPC or a 3,6-di-Br-PEPC solution in acetone and V₂O₅ water sol (V₂O₅ sol was obtained by the Bilts method). The composites were synthesized in the following way: a) sol of 0.16 wt.% V₂O₅ concentration was added into a 0.14 wt.% polymer concentration PEPC solution in acetone at different

(1:1, 1:2, and 1:3) volume ratios corresponding to 33.82, 48.33, and 52.80 wt.% V_2O_5 contents in composites, respectively; b) sol of 0.16 wt.% V_2O_5 concentration was added into a 0.16 wt.% polymer concentration 3,6-di-Br-PEPC solution in acetone at different (1:1, 1:2, and 1:3) volume ratios corresponding to 24.80, 38.00, and 42.67 wt.% V_2O_5 contents in composites, respectively.

The films were formed as “sandwich” structures by pouring the PEPC+ V_2O_5 or 3,6-di-Br-PEPC + V_2O_5 composites, respectively, onto a glass substrate covered with a layer of sputtered ITO and a resistance about 100 Ohm/ \square . When dried in air at room temperature, the composite films were 5 to 10 μm thick. For other contact, In of ~ 1 mm thick and the 1-mm² working surface was used by pressing method. Alongside the formation of the above films, the powders of the PEPC + V_2O_5 and 3,6-di-Br-PEPC + V_2O_5 composites (at the same ratio of components) were prepared to elucidate a possibility of intercalation of PEPC and 3,6-di-Br-PEPC into interlayer galleries of V_2O_5 . Filtered CuK α -emission DRON-3M diffractometer’s X-ray diffractograms show no intercalation of PEPC and 3,6-di-Br-PEPC into interlayer galleries of V_2O_5 . The interlayer distances in V_2O_5 were 11.55 Å both for net V_2O_5 xerogel and PEPC+ V_2O_5 and 3,6-di-Br-PEPC+ V_2O_5 composites. The absence of PEPC and 3,6-di-Br-PEPC intercalation into V_2O_5 is, evidently, attributed to the great size of polymers owing to space carbazole substitutes in the polymer’s chain in contrast to linear ones having no polyaniline substitutes [6]. The measurements of quasi-static CVC were performed by a 14 TKC-100 automated tester with 0.2% error for voltage and 0.5% for current following the standard technique [9–11] in dark and under illumination of samples by non-filtered light from an A-type source with a color temperature of 2850 °C. The obtained CVC were then processed by a differential method [9–11]. The relationship order of current values in dark and under illumination were calculated from the corresponding CVC.

2. Results and Discussion

The CVCs of PEPC and 3,6-di-Br-PEPC based structures in dark in the voltage range from 0.1 to 10 V as well as changes in current at 1 V depending on the V_2O_5 concentration are shown in Fig. 1. The curves demonstrate that the increase of the nanosized V_2O_5 content in PEPC up to 48.33 wt.% leads to the current increase that should be attributed to the interaction of V_2O_5 with two neighboring carbazole fragments in

the PEPC polymer chain to form the donor-acceptor complex [PEPC^{+ δ} ... V_2O_5 ^{- δ}], in which V_2O_5 acts as an electron acceptor. This confirms the shift of the PEPC absorption band (max=330 nm) towards the 450–500 nm visible region when the insertion of V_2O_5 into the polymer as well as the appearing of a luminescence band with max=520÷525 nm. Probably, V_2O_5 forms a bridge between two neighboring carbazole fragments and thus facilitates the conduction in PEPC+ V_2O_5 films (33.82 and 48.33 wt.% of V_2O_5 content) (Fig. 1, *a, c, e, f*) as compared with that of PEPC, in which the current was considerably lower in this voltage range. With a further increase in the V_2O_5 concentration to 52.80 wt.%, the current decreases (the film conduction decreases) (Fig. 1, *a, c, e, f*, curve *3*). The observed decrease of the current can be, probably, interpreted in this case by the presence of impurity centers due to the V_2O_5 excess alongside with the formation of donor-acceptor complexes [PEPC^{+ δ} ... V_2O_5 ^{- δ}]. The stated centers act as traps for electrons and promote the recombination of charge carriers. Such a phenomenon was observed for PEPC: V_2O_5 at both polarities (Fig. 1, *c, f*, curves *1*). Such a behavior can be also attributed to the effect of the recombination processes in the films under research. An increase in the concentration of nanosized V_2O_5 leads to smaller distances between centers formed by V_2O_5 . At the initial V_2O_5 concentration of 33.82 wt.%, the increase of conduction is due to increasing the thermal generation of carriers from inserted centers. With a further increase in the V_2O_5 concentration, the concentration of current carriers was observed to increase alongside with raising the probability of their recombination depending on the bias applied as well. Note, Onsager and Pope [12, 13] reported that the probability of the separation of a thermalized electron-hole pair dependent on the applied voltage. For instance, for the probability to avoid the initial recombination with a parent ion to be equal to 0.7, the initial electron-ion separation in the outer field of 10³ V/cm should be equal to 450 Å. Whereas for 10³ V/cm field, the ~ 80 Å distance is quite sufficient to attain the same probability. Obviously, just increasing the recombination with increasing the V_2O_5 concentration in charge carriers (curve *3*, Fig. 1) is a main reason for the reducing in CVC. A more sharp slope in CVC (α) with increase in the voltage is one more evidence in benefit of this pattern of the V_2O_5 concentration effect on CVC. To confirm this suggestion, further investigations are to be carried out. For composite films 3,6-di-Br-PEPC: V_2O_5 with the V_2O_5 content equal to 24.8, 38.00, and 42.60 wt.%, other current-voltage relationship was

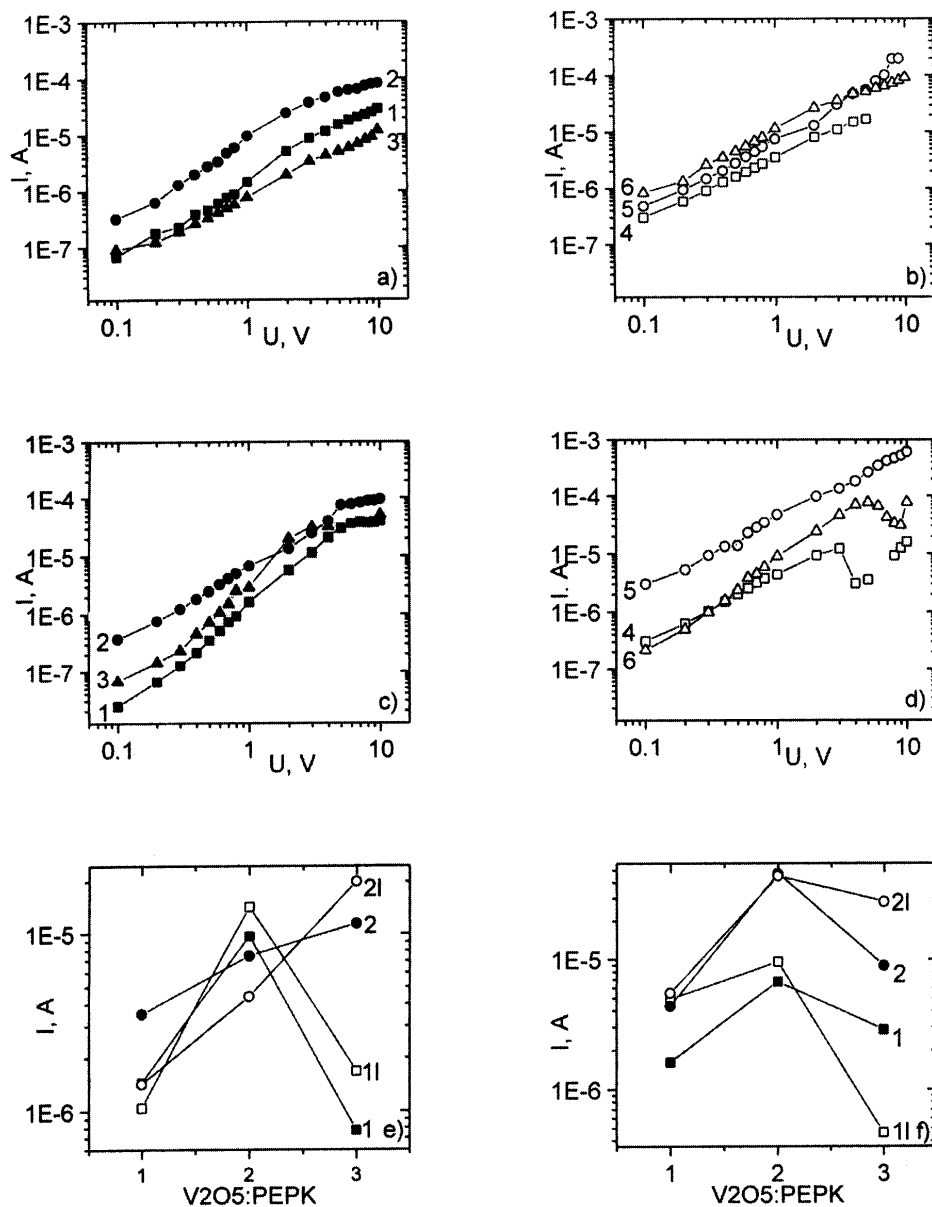


Fig. 1

observed with increase in the V_2O_5 concentration (Fig. 1, b, e). When the bias “+” is applied to In, with increase in the V_2O_5 content up to both 38.00 and 42.60 wt.%, the current grows in contrast to PEPC: V_2O_5 (Fig. 1, a). Such a different behavior of CVC can be attributed to the lesser electron-donor ability of 3,6-di-Br-PEPC as well as space barriers due to the formation in carbazole fragments in sites 3,6 of hydrogen atoms for bromine atoms. Owing to this fact, more weak non-stable complexes with charge transfer [3,6-di-Br-PEPC $^{+\delta}$... $V_2O_5^{-\delta}$] as compared with non-substituted

PEPC are formed. For the equilibrium shift to form such a complex, a higher V_2O_5 concentration is needed. When applying the bias of polarity “-” to In, we observed the same behavior as that for PEPC: V_2O_5 (Fig. 1, f).

A similar situation was observed in all cases where films were illuminated with unfiltered light of the A source with a color temperature of 2850 °C (Fig. 2, e, f).

An interesting peculiarity of the CVC behavior is that, at the V_2O_5 minimum content for both composites (33.82 and 24.80 wt.%, respectively), the ratio of the currents under illumination and in dark $k = I_{\text{light}}/I_{\text{dark}}$

is practically a stable value in both cases: $k > 1$ with the “-” bias applied to In and $k < 1$ with “+” polarity (Fig. 2, a, b). An essential increasing of this value, when “-” polarity, especially for films with a V_2O_5 content of 33.82 wt% in PEPC, is evidently attributed to the domination of the injection of majority charge carriers over the injection of minority carriers. In this case, the ratio k is not a stable value (Fig. 2, c), but with $k > 1$ both for “-” and “+” polarities on In. As shown in Fig. 2, c, the ratio of currents under illumination and in dark reaches its maximum $k=7$ in the case of the maximum V_2O_5 content in 3,6-di-Br-PEPC with “-” polarity. Meanwhile for PEPC, the maximum $k=3$ is achieved at a minimum V_2O_5 content and the same polarity.

Thus, in order to increase the photosensitivity of these structures, the following is necessary:

1) to use “-” polarity of the applied bias on In, since a level of the injection of minority carriers is lower in this case;

2) to use polymer composite films with the maximum content of V_2O_5 in 3,6-di-Br-PEPC and the minimum one in PEPC.

On the other hand, such a situation shows the more pronounced domination of majority carriers over minority ones at “-” polarity, than in the case of “+” polarity. Such a phenomena is due to the fact that the injection of minority current carriers causes reducing the photosensitivity and ratio [9–11] which is observed when the “+” polarity is applied to In. The differential processing of CVC on the log-log scale as $\alpha = d \lg I / d \lg U$ allowed us to reveal the uncommon behavior of CVC of the structures under research. The processing results demonstrate that α is not a constant value and does not depend on such parameters as the V_2O_5 concentration, illumination, and polarity. The maximum value of α varies from 1 to 2.5 at the applied voltage of 1–10 V (Fig. 3). The curves have some sectors with $\alpha = 1.25$, which is evidently intrinsic to polymers and non-ordered structures on the whole. But until now, we do not know the mechanism of a current flow for this value of α . Generally, while observing the dependence on the V_2O_5 concentration, it is rather difficult to determine a certain mechanism of the current flow in these structures. Thus, for example, the bimolecular recombination shows $I \sim U^{1.5}$; the monomolecular one shows $I \sim U^2$; currents limited by a space charge in trapless dielectrics — $I \sim U^2$ [9]; currents in polymers with small traps — $I \sim U^{2.5}$ [12]; and, at high levels of the injection in dielectrics — $I \sim U$ [9, 14].

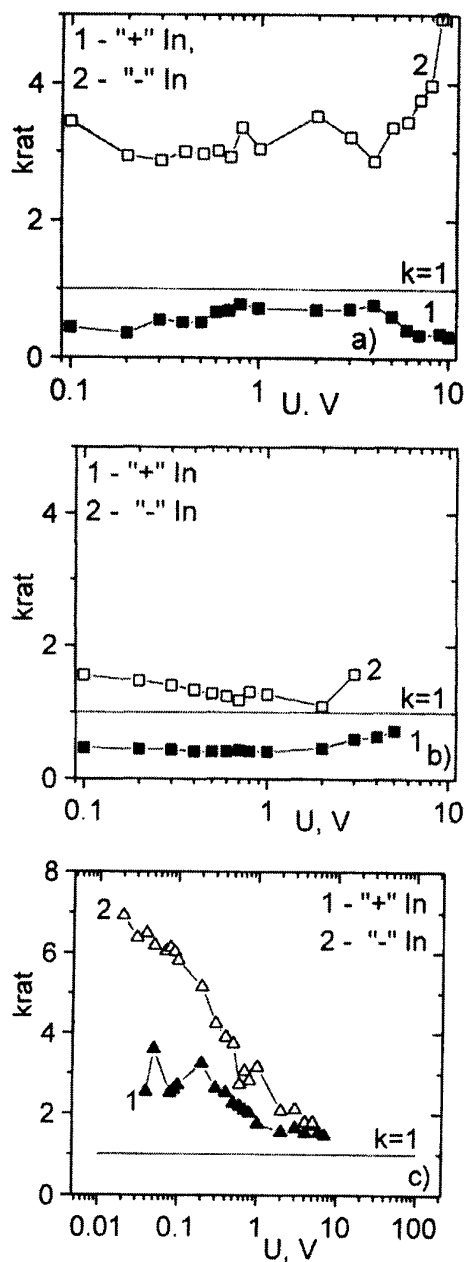


Fig. 2

Conclusion

The study of CVC of the “sandwich”-type structures based on PEPC and 3,6-di-Br-PEPC with V_2O_5 nanosized particles has resulted in the following:

1) The effect of V_2O_5 concentration in PEPC composite on CVC has a non-monotonous character. The 48.33 wt.% content of V_2O_5 in PEPC was found to be optimum to attain the maximum conduction at

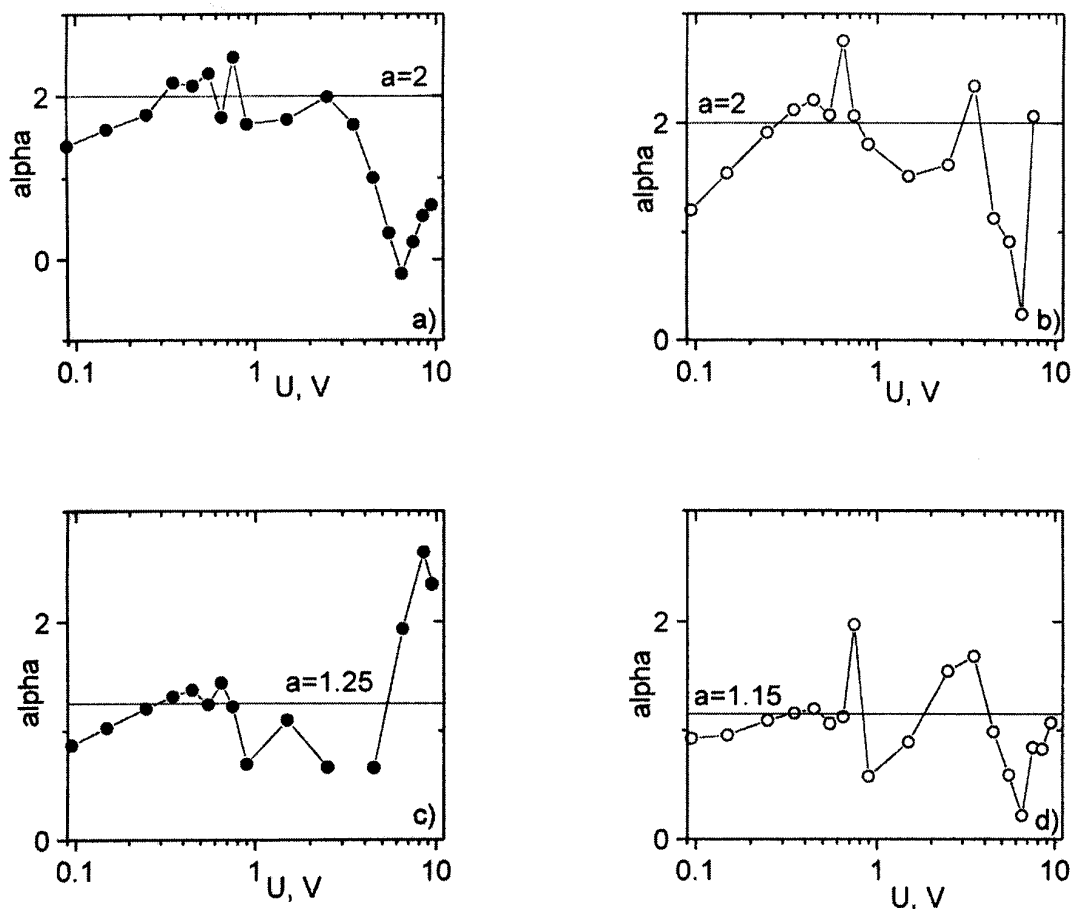


Fig. 3

each polarity. The effect of V_2O_5 concentration in 3,6-di-Br-PEPC polymer has the same character for “-” polarity on In. However, when “+” polarity on In, then the max V_2O_5 concentration is needed to attain the maximum conduction.

2) The maximum ratio of the currents under illumination and in dark is observed for the structures based on 3,6-di-Br-PEPC with maximum concentration; PEPC-based structures have their ratio to be maximum at the V_2O_5 minimum concentration. The maximum photosensitivity was observed at low voltages (below 1 V) (Fig.2,c) and negative polarity on In.

3) The differential slopes of CVC under illumination and in dark have no certain regularities of changes; for every special case, α has a maximum from 1 to 2.5 varying with voltage changes. CVC plots have sectors with $\alpha = 1.25$. Presumably, it is generally intrinsic to polymeric and non-ordered structures.

Some peculiarities of the charge flow in “sandwich”-type structures based on polymer composite films PEPC

and 3,6-di-Br-PEPC with V_2O_5 nanosized particles have been studied. The increase of the V_2O_5 concentration in the polymer was found to non-monotonously influence CVC except the case for 3,6-di-Br-PEPC at “+” polarity applied on In. The maximum photosensitivity was found for the structures, when negative polarity applied on In: for PEPC with the minimum concentration of V_2O_5 of 33.82 wt.% and for 3,6-di-Br-PEPC with the maximum concentration of V_2O_5 of 42.67 wt.%. It was shown that the differential slope of curves is not definitely dependent on the V_2O_5 concentration, polarity, or illumination reaching a value from 1 to 2.5 in every special case. Some sectors of CVC curves have $\alpha = 1.25$, which is evidently intrinsic to polymers and non-ordered structures.

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ЕЛЕКТРИЧНІ ТА ФОТОЕЛЕКТРИЧНІ ВЛАСТИВОСТІ ПЛІВОК НА ОСНОВІ РЕРС ТА 3,6-ди-Вг-РЕРС З НАНОЧАСТИНКАМИ V₂O₅

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Резюме

Досліджено особливості транспорту заряду в “сандвіч” структурах ІТО/композит/Іп на основі плівок з полімерів РЕРС (поліепоксипропилкарбазол) або 3,6-ди-Вг-РЕРС і наночастинок V₂O₅. Збільшення концентрації V₂O₅ в полімерній плівці немонотонно впливає на вольт-амперні характеристики (ВАХ), за винятком прикладення додатної напруги на 3,6-ди-Вг-РЕРС. Максимальна фоточутливість спостерігається для структур РЕРС з мінімальною концентрацією V₂O₅ (33,82 ваг.%) та 3,6-ди-Вг-РЕРС з максимальною концентрацією (42,67 ваг.%) при негативному потенціалі на Іп електроді. Диференціальний нахил кривих α не залежить від концентрації V₂O₅, полярності, чи освітлення; але змінюються при збільшенні напруги від 1 до 2,5 В. В більшості випадків $\alpha = 1,25$, що характерно для полімерів та невпорядкованих структур.