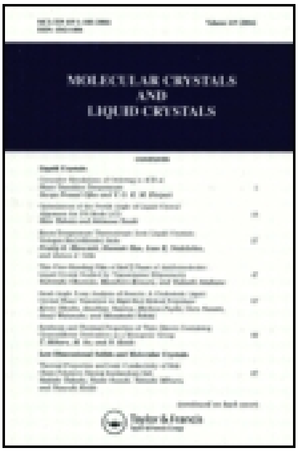

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Experimental Study of CU/TCNQ Composites Formed by Charge-Transfer Reaction in Acetonitrile

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EXPERIMENTAL STUDY OF CU / TCNQ COMPOSITES FORMED BY CHARGE-TRANSFER REACTION IN ACETONITRILE

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Abstract We present here a comparative study of the electrical properties of two series of Cu / TCNQ composites, respectively with, and without, significant charge-transfer between Cu and TCNQ.

Keywords: Cu/TCNQ composites, charge transfer reactions, electrical properties, solid-solid reactions

INTRODUCTION

The ability of organic π-electron acceptor TCNQ (tetracyanoquinodimethane), to form, in solution, conducting charge-transfer crystals with a high number of organic or metallic donors, is well known for a long time [1-2].

Some of these charge-transfer reactions are metathetical reactions in which one (at least) of the two moieties is already in an ionic form. This is the case, for instance, for the reaction between TCNQ and lithium iodide (Li^+I^-) which produces the salt Li^+TCNQ^- together with free iodine [1].

In other cases, however, the reaction is a direct oxidation-reduction process between two initially neutral moieties[1-2]. Two representative examples are: 1) the reaction between TCNQ and TTF (tetrathiafulvalene) [3], and 2) the organo-mineral reaction between TCNQ and metallic copper.

In the present paper, we report on an investigation of charge-transfer reaction, obtained in presence of acetonitrile (CH_3CN), between metallic copper and TCNQ. Right proportions of the two powdered components are first allowed to react in presence of solvent. Then, the product of the reaction is dried and compacted for electrical measurements.

DC electrical conductivity, activation energy and thermopower data, are presented as a function of the copper concentration. These data are complemented by an infrared study. The observed properties are discussed in comparaison to those of non interactive mixtures obtained between Cu and TCNQ, in absence of solvent, just by slightly pounding the two components together in a mortar. Some percolative aspects of the electrical conduction at low copper concentration are also presented.

RESULTS AND DISCUSSION

TCNQ is first purified by two crystallisation stages in CH_3CN. Metallic copper is in the form of a fine electrolytic powder, with 99 % purity and 50 µm maximum grain size. The experimental study is made here according to a standard procedure already described by us in several papers [4-5-6].

We have demonstrated in the past that a well defined peak at 825 cm^{-1} in the powder infrared spectra of TCNQ salts and TCNQ composites could be used as a sensitive indicator of the amount of anionic species TCNQ$^-$ present in the material [7]. In neutral TCNQ, the corresponding peak is observed at 863 cm^{-1}. In other words, the observation of the peak at 825 cm^{-1} in a material is a clear proof of the occurence of a charge-transfer reaction.

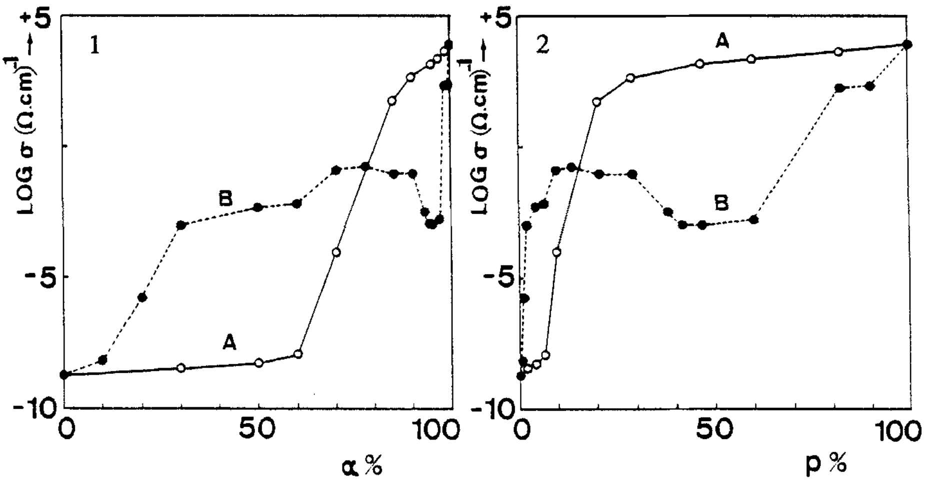


FIGURE 1 Electrical conductivity of Cu / TCNQ composites /A/ and /B/, versus α, the molar fraction of Cu.

FIGURE 2 Electrical conductivity of composites /A/ and /B/, versus p, the volume fraction of Cu.

In the case of those Cu / TCNQ composites which are formed in absence of solvent, named thereafter composites /A/, the characteristic peak at 825 cm^{-1} is unobserved, whatever the concentration of copper is. Therefore, it must be concluded that composites consist, in this case, of non-reactive mixtures.

The room temperature DC electrical conductivity σ of composites /A/ (compaction pressure: 2.4 Kbars), is reported on a logarithmic scale, as a function of the molar fraction α of copper, Figure 1A, on one hand, and of the volume fraction p of copper, Figure 2A, on the other. One notices that these two representations are quite different. This is due, primarily, to the large disparity in specific masses of components Cu and TCNQ. The reported behaviour of σ in fig.2A closely resembles that of a macroscopically heterogeneous non-interactive medium consisting of a "conductor", with conductivity σ_1, and an "insulator", with conductivity σ_2. Those volume fractions are p and 1-p, respectively . Electrical conduction in such a medium is adequately described by standard percolation theory [8]. According to this theory, the macroscopic conductivity σ_M, in the conducting régime: $p > p_c$, near p_c, and in the limit appropriate here: $\sigma_2 << \sigma_1$, obeys a power law of the form:

$$\sigma_M = \sigma_1 (p - p_c)^t$$

When direct application of this law to the σ-data of fig.2A is attempted, the best fit results from the following values of parameters:

$p_c = 0.10$

$\sigma_1 = 7.1 \times 10^3 (\Omega x cm)^{-1}$

$t = 1.6$

This fit, not shown in fig.2A, is reasonably good (even up to p = 1, for which limit the above law gives: $\sigma_M = 0.84\ \sigma_1$, instead of the true value σ_1). One must however keep in mind that strong differences exist between mechanical properties of the two components: (mass density, hardness, shape and size of grains...) which can have a crucial influence on the parameters of the theory.

We now describe the results of a second set of experiments performed on a new series of composites, or composites /B/, having the same composition as composites /A/, but in which the charge-transfer interaction between Cu and TCNQ is now produced by adduction of solvent CH_3CN. More precisely, an excess of CH_3CN is introduced into the mixtures containing the right proportions of solid Cu and TCNQ, in order to dissolve all the organic component. A spontaneous blackening is then observed as a proof of occurrence of the reaction. The mixtures are afterwards allowed to dry by evaporation of solvent in ambient air and directly utilized (without any subsequent grinding) in the form of standardized pellets compacted under 2.4 Kbars.

The conduction behaviour of composites /A/, reported in fig.1 and fig.2, and described in the preceding section, is primarily attributable to the physical structure of these composites. Therefore, it seems more appropriate, in this case, to report the σ-data as a function of the volume fraction p of copper. On the contrary, in the case of composites /B/, which are formed in presence of CH_3CN, the electrical behaviour depends primarily on the occurence of a chemical charge-transfer reaction. Consequently, one should consider, in this case, the molar fraction α of copper to be a more convenient parameter for representing the σ-data.

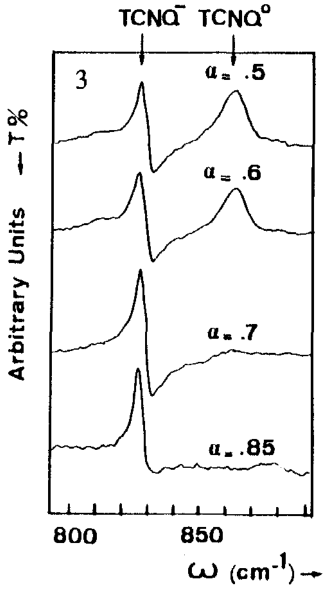
The charge-transfer reaction, involved in the formation of composites /B/, is, in its simplest form:

$$\alpha Cu^0 + (1-\alpha)TCNQ^0 \rightarrow \alpha Cu^+TCNQ^- + (1-2\alpha)\,TCNQ^0 \qquad \text{if } \alpha < 0.5 \qquad /1a/$$

$$\alpha Cu^0 + (1-\alpha)TCNQ^0 \rightarrow (1-\alpha)Cu^+TCNQ^- + (2\alpha-1)\,Cu^0 \qquad \text{if } \alpha > 0.5 \qquad /1b/$$

However, we always observe that only some fraction f (<1) of free copper is involved in the charge-transfer process, whatever α is. This point will be commented later on, but, for instance, reaction /1a/ with $\alpha < 0.5$, should be more correctly written:

$$\alpha Cu^0 + (1-\alpha)TCNQ^0 \rightarrow \alpha f Cu^+TCNQ^- + \alpha(1-f)Cu^0 + (1-\alpha-\alpha f)TCNQ^0 \qquad /2/$$



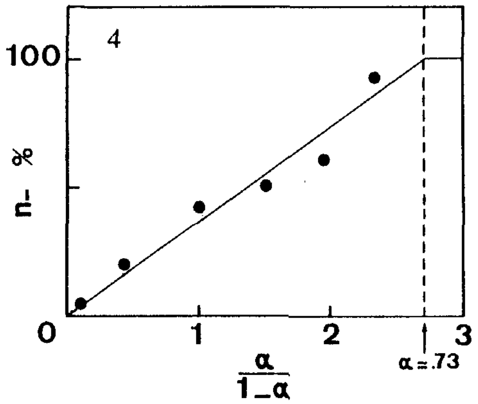


FIGURE 3 Examples of infrared structures characterizing $TCNQ^0$ and $TCNQ^-$, in the particular frequency range between 800 and 900 cm^{-1}.

FIGURE 4 Experimental fraction n_- of $TCNQ^-$ versus $\alpha/(1-\alpha)$, for composites /B/, deduced from the infrared spectra, as indicated in the text.

An evaluation of the fraction f of oxidized copper can be achieved, for different values of α, by means of infrared spectroscopy, on KBr pellets of the composites. From relative oscillator strengths of the two resonances at 863 cm^{-1} for $TCNQ^0$ and at 825 cm^{-1} for $TCNQ^-$, already determined in a previous work [9], and from integrated intensities of the corresponding IR absorption bands, Figure 3, one may deduce the respective fractions: $n_0 = N_0/N$ and $n_- = N_-/N$, of neutral (^{0}) and reduced ($^-$) TCNQ molecules ($n_0 + n_- = 1$).

The latter fraction may also be written as: $n_- = \alpha f/(1-\alpha)$, according to the above reaction /2/, and, thus, it may be utilized to evaluate f as a function of α.

The results of such a procedure are shown in Figure 4, in the particular form: n_- versus $\alpha/(1-\alpha)$. In view of these data, it may be reasonably concluded that such a dependence is linear. In other words, one may infer from the results of fig.4 that the fraction f of oxidized copper is essentially independent of the total fraction α of copper introduced in the composites. Within this approximation, the corresponding value of f can be simply evaluated from a linear least mean square fit of the data. One obtains numerically, in this way: $f = 0.365$.

The above result, with $f<1$, clearly indicates that the copper grains are only partly oxidized during the reaction process, namely to 36.5%, on the average. This particular value is a probable consequence, at least in part, of our experimental procedure and, more especially, of grain size distribution in Cu powder utilized to form the composites. We did not attempt, in the present study, to re-grind these composites in presence of an additional amount of solvent, althought we believe that the yield of the charge-transfer reaction could well be improved in this way.

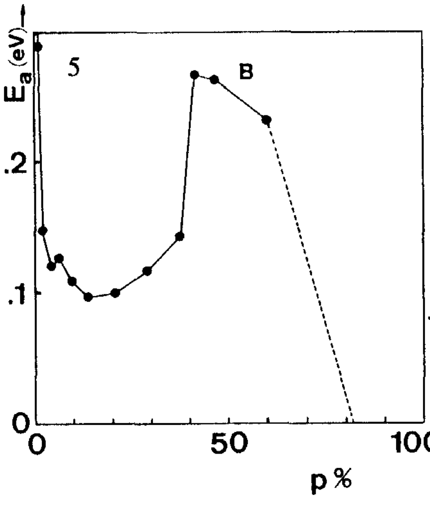
The room temperature DC electrical conductivity σ_B of composites /B/ (also compacted under 2.4 Kbars) is reported, on a logarithmic scale, as a function of the volume fraction p of copper in fig.2B (p stands always for the volume fraction of free copper initially introduced in the composites) and as a function of molar fraction α in fig.1B.

One may start a discussion of these results, considering that the net effect of the charge-transfer reaction is to introduce a third component in the composites. The electrical conductivity of this component should be both considerably smaller than those of pure Cu metal ($\sigma \approx 5.5\ 10^3\ (\Omega.cm)^{-1}$) and considerably higher than those of pure TCNQ insulator ($\sigma \approx 2\ 10^{-9}\ (\Omega.cm)^{-1}$), all these conductivities being measured in the same conditions. One may take, as a reference for this third component, the conductivity of the stoichiometric salt: Cu(I)TCNQ: $\sigma \approx 3\ 10^{-2}\ (\Omega.cm)^{-1}$, or even those of the salt: Cu(II)TCNQ: $\sigma \approx 4\ 10^{-3}\ (\Omega.cm)^{-1}$ [10].

These different orders of magnitude provide a natural explanation to the fact, shown in figs.1 and 2, that $\sigma_A > \sigma_B$, near $\alpha = 1$, and $\sigma_A < \sigma_B$, near $\alpha = 0$. However, the much steeper decrease of σ_B observed as α decreases from its maximum value, is still somewhat intriguing. The simplest explanation might be to consider that the charge-transfer reaction is able to spread over the whole surface of Cu grains, even when there is a large excess of copper, owing to the fact that the second component, TCNQ, is acting in solution. After evaporation of solvent, this results into the formation of very thin solid shells of the (poorly conducting) charge-transfer product which cover all Cu grains and insulate them electrically from each other.

Still more intriguing is the fact that σ_B attains a deep minimun for $\alpha = 0.93$, and, then, starts to increase when α is decreased again. One may notice that this minimum corresponds also, approximately, to equal volumes of free components, or to $p = 0.50$, in the mixture. Thus, σ_B is observed to increase by two orders of magnitude, when α decreases from 0.93 to 0.80, attaining a broad maximum at this latter value. We do not have any satisfying explanation for this particular behaviour.

For $\alpha < 0.80$, σ_B decreases continuously, as α goes to 0, through some broad structure, and an edge-like structure, possibly attributable to a percolation threshold, is observed near $\alpha = 0.2$.



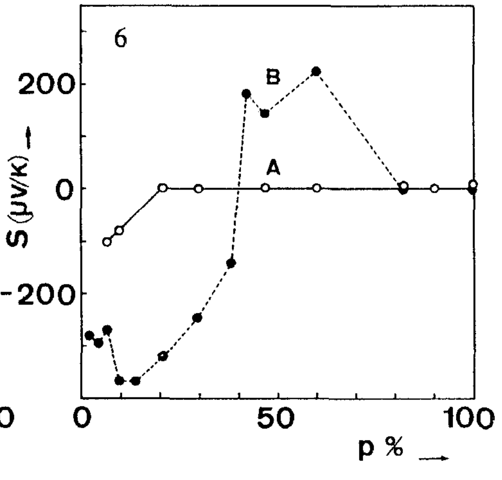


FIGURE 5 Activation energy for DC electrical conductivity of composites /B/, near 300 K, versus the volume fraction p of copper.

FIGURE 6 Thermoelectric power of composites /A/ and /B/, near 300 K, versus the volume fraction p of copper.

Activation energy data are also presented in fig.5, in complement to electrical conductivity data. These data result from an experimental study of σ_B performed between 100 and 300 K for various α-compositions. The activation energy E_a is, as usual, deduced from logarithmic plots of σ_B versus reciprocal temperature. All the plots so obtained are almost linear and thus, characteristic of a thermally activated process of the form: $\sigma_B(T) = \sigma_{B0} \exp(-E_a/kT)$, in which σ_{B0} is some pre-exponential factor and k, the Boltzmann constant.

At fixed temperature, for instance: T = 300 K, and if σ_{B0} does not vary with α, the above expression leads to identical behaviours for the α-dependences of both $L\sigma_B$ and E_a. In the present case, there is no reason to consider: $\sigma_{B0}(\alpha)$ = constant, however, it is clear, from fig.2 and fig.5, that there exists a significant correlation between the α-dependences of E_a and of $L\sigma_B$ at room temperature, although the two behaviours can not be simply identified.

Figure 6 presents experimental data of thermopower S measured on composites /A/ and composites /B/ previously defined. Curve (A) is representative of a non-interactive heterogeneous medium formed partly of a conductor and partly of an insulator. For $p > p_c$, both the positive sign and smallness of thermo-emf are in good agreement with the metallic properties of copper [11]; whereas for $p < p_c$, the behaviour of S becomes quite different, being rather like that of an insulator ruled by impurities. On curve (B), one observes a very large spreading of the S-values, from +246 μV/K to -368 μV/K, with a change in the sign of S, i.e. in the nature of the majority carriers, occuring near $\alpha = 0.93$ or $p = 0.38$. Such a variation is considerable at the scale of the S-values for metallic copper, typically of the order of 1 μV/K at 300 K [11]. From these data it may be inferred that positive carriers are associated to the low conductivity and high activation energy régime occuring in the α-range from 0.93 to 0.97. Afterwards, i.e. for $\alpha > 0.97$, the observed behaviour is roughly that of metallic copper.

At last, comparison may be made with the corresponding values of E_a and S, measured on powders of the two stoichiometric salts: Cu(I)TCNQ and Cu(II)TCNQ [10]. These values are: 0.11 eV and -280 μV/K for the first-one, and 0.13 eV and +305 μV/K for the second-one. The striking difference that exists between these two thermo-emf-values is still unexplained.

CONCLUSION.

Some experimental results on the electrical properties of two series of Cu / TCNQ composites formed directly from Cu and TCNQ powders, respectively with and without adduction of solvent, have been presented and discussed. These results are primarily governed by the particular grain size distribution of Cu powder utilized here (< 50 μm).

A new study involving composites formed from a much more divided Cu powder (submicron grain size) is presently in progress.

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