

SPACE-CHARGE-LIMITED CURRENTS IN POLY-N-VINYLCARBAZOLE FILMS

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The space-charge-limited currents in poly-N-vinylcarbazole films were investigated with the use of electrolytic solutions such as Ag^{2+} in 7.5N HNO_3 , NaI solution saturated with iodine, and Ce^{4+} in 15N H_2SO_4 . These oxidizing solutions are suitable hole-injecting electrodes. The current-voltage characteristic indicates the existence of exponentially-distributed traps, the concentration of which is about $5 \times 10^{18} \text{cm}^{-3}$.

The studies on the space-charge-limited (SCL) currents provide many useful informations regarding traps in insulators.¹⁾ Although many investigations have been made in organic molecular crystals such as anthracene²⁾ and naphthalene,³⁾ there are few studies on the traps in polymers. One of the important things for a better understanding of the electrical properties in polymers is to know the influence of traps, since there seem to be many traps in amorphous polymers. Traps in polymers are roughly due to two causes, i.e., impurity and structural origin, because of the difficulty of purification and the low crystallinity of polymers.

Concerning the traps in poly-N-vinylcarbazole (PVK) film, the studies on the activation energy of dark- and photo-currents suggested the existence of both deep and shallow traps,⁴⁾ and the studies on the thermally stimulated currents showed that the uniformly distributed traps lie between 0.66 and 0.77 eV above the valence band.⁵⁾ The details are, however, still unknown.

The present paper shows the preliminary results on the SCL hole-current in PVK films with the use of the electrolytic injecting electrodes. The experimental results suggest the existence of exponentially-distributed traps in PVK films.

EXPERIMENTAL

The PVK was obtained from radical polymerization of vinylcarbazole in a benzene solution with AIBN catalyst, and was purified by repeated reprecipitations from benzene solution with distilled methanol. For the preparation of film, a benzene solution containing desired quantity of PVK was deposited on a quartz plate and the solvent was slowly evaporated in a vessel saturated with solvent vapor at room temperature. The film was stripped from the plate by edging the hem of the film and dipping it in distilled water, and dried in vacuo.

For the measurement of injection currents, a similar cell to the Pope-Kallmann cell⁶⁾ was used. One electrode compartment was filled with an electrolytic solution ($\text{Ag}^{2+}/7.5\text{N } \text{HNO}_3$, NaI solution saturated with iodine, or $\text{Ce}^{4+}/15\text{N } \text{H}_2\text{SO}_4$)⁷⁾ which injects holes into PVK films, and the other was filled with a 1M aqueous solution. The voltage was applied between two platinum electrodes in these compartments. The contact area of hole-injecting electrode was 0.031cm^2 .

RESULTS AND DISCUSSION

In the measurements of the SCL currents, it is a serious problem to find a suitable injecting material to make an ohmic contact. The energy condition for a hole-injecting contact to be ohmic is $\phi \simeq I_p$, where ϕ denotes the work function of the electrode and I_p the energy required to remove an electron from the valence band of the material into the vacuum. In the case of organic materials,

however, this condition can hardly be achieved with ordinary metals or semiconductors because of their higher ionization potential and smaller polarization energy, but can be achieved with electrolytic solutions.

We have attempted the injection of holes into PVK films with three electrolytic solutions described in the experimental section. Possibility of hole injection into PVK films from these electrodes was provided from the ESR studies. When PVK films contacted with these oxidizing solutions, the color of films changed brown. After the brown-colored films were washed with water and sealed in a quartz-tube under vacuum, the ESR absorption spectra were measured. Figure 1 shows the ESR absorption spectra of these brown-colored films. All the samples show the ESR signal with a g -value of about 2.005, indicating that the radical species are formed on the surface of PVK films by the contact with these solutions. Compared with the results of the ESR studies of γ -irradiated PVK⁸⁾ and the ESR studies of the charge-transfer complexes of PVK,⁹⁾ the radical species seem to be cation radicals of PVK. It is well known that the presence of the paramagnetic radical ions formed in connection with the electron-donor-acceptor complexes is necessary for the hole injection,¹⁰⁾ although the detailed mechanism of the production of free holes from these radical species is still unknown.

With the use of these electrolytic solutions, the injection currents were measured as a function of applied voltages. Figure 2 shows the results observed for the forward current versus applied voltage. We could not obtain a reliable current-voltage curve with the use of Ag^{2+} solution, because the oxidizing ability changes with time and the color of the solution disappears. The current-voltage curve is ohmic at lower fields and superlinear at higher fields, although the transition from ohmic to superlinear behavior is not so clear. The current-voltage curve at higher fields fits the relation, $j \propto V^3$, which is typical for the SCL currents assuming the existence of an exponential trap distribution.

In order to obtain another evidence for the observed current to be space-charge-limited, the thickness dependence of the current was investigated at various voltages. Figure 3(b) shows the plot of the observed current at the superlinear region versus the thickness (d) of the film. The currents fit the relation, $j \propto d^{-L}$ ($L = 5 \sim 6$). This result indicates that the observed current is not only volume-controlled but space-charge-limited.

According to Mark and Helfrich,¹¹⁾ the SCL current in the presence of exponentially distributed traps follows the relation;

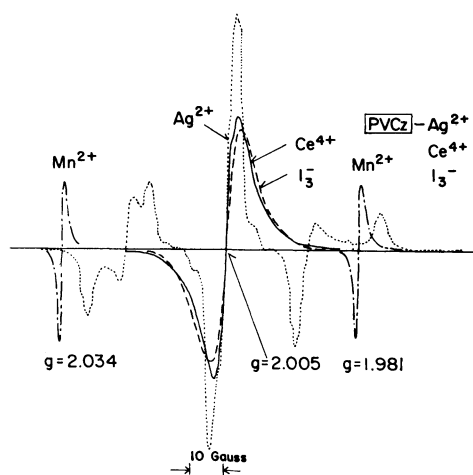


Fig.1. ESR absorption spectra of complexes formed between PVK and oxidizing agents in the solid state.

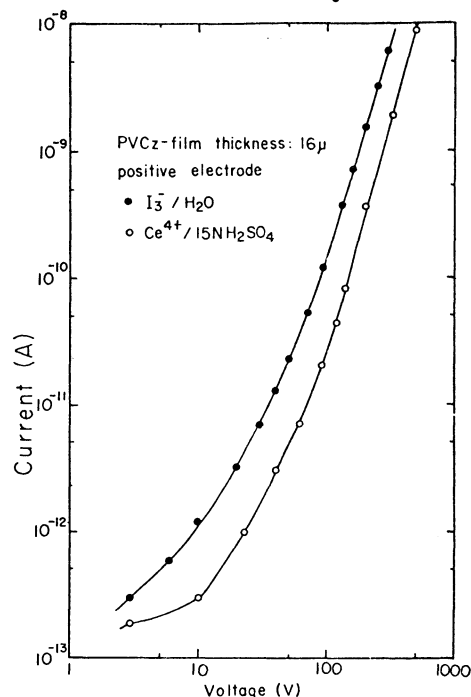


Fig.2. Current-voltage characteristics with the use of electrolytic injecting electrodes.

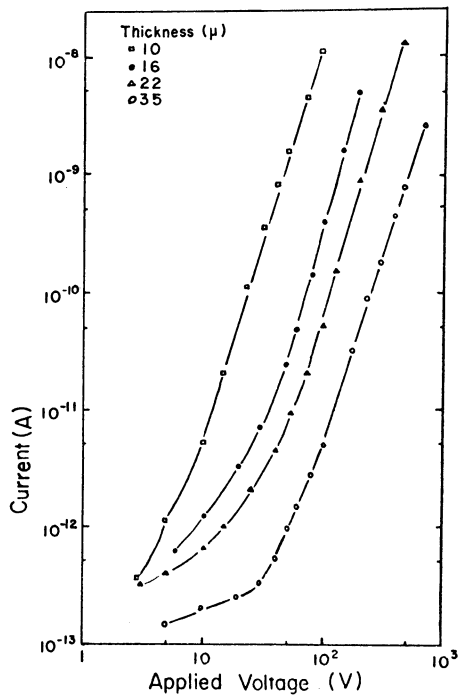


Fig. 3(a). Current-voltage characteristic as a function of film thickness.

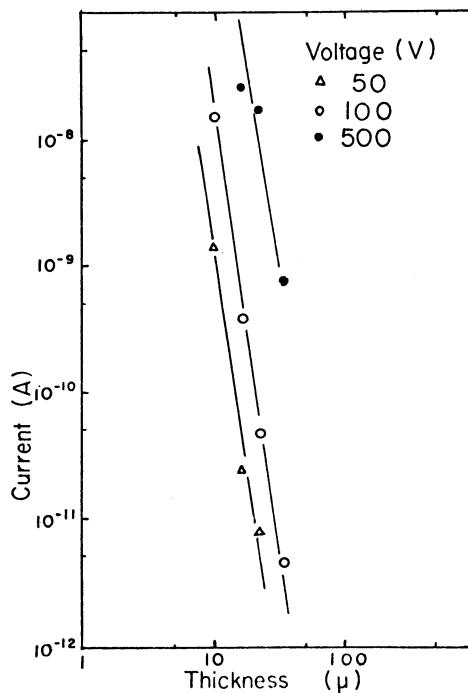


Fig. 3(b). Thickness dependence of the currents at various voltages.

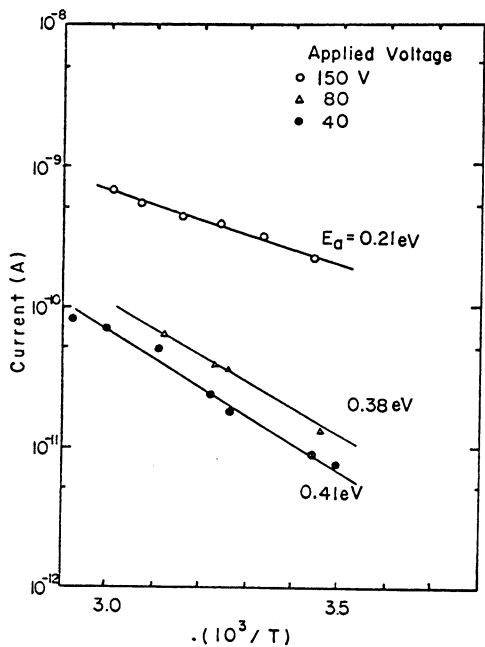


Fig. 4. Temperature dependence of the SCL hole current.

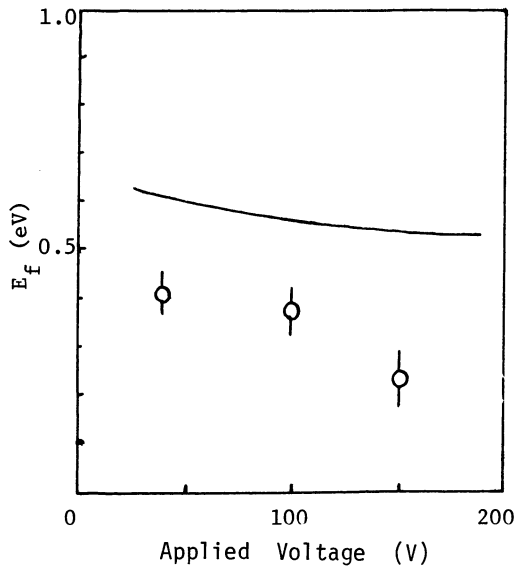


Fig. 5. Activation energy of the SCL hole current versus applied voltage. The solid line represents the calculated values of E_f with $d=20 \mu$, substituting $\mu=10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ reported by Gill¹²⁾ and $H_0=5 \times 10^{18} \text{ cm}^{-3}$ obtained from the present data with $L=2$ in equation (1). The open circles represent the experimentally obtained value of activation energy.

$$j = N_0 \mu e^{1-L} \left(\frac{\epsilon \epsilon_0 L}{H_0 (L+1)} \right)^L \left(\frac{2L+1}{L+1} \right)^{L+1} \left(\frac{V^{L+1}}{d^{2L+1}} \right) \dots \dots \dots (1)$$

N_0 is the effective density of states in the band (valence band or conduction band), e the electronic charge, ϵ the dielectric constant, H_0 the total trap concentration, d the thickness of samples, μ the mobility, V the applied voltage, and $L=T_c/T$ where T_c characterizes the trap distribution.

Now assuming $L=2$, the current should be proportional to the cubic power of the voltage and also inversely proportional to the fifth power of the thickness. These power dependencies agree well with the experimental results.

Further, if we assume the extreme case that the SCL hole current is controlled only by exponentially distributed traps in PVK films, it is expected that the quasi-Fermi-level moves toward the valence band with increasing applied field and that the apparent activation energy decreases with increasing applied field. As shown in Fig.4, the activation energy decreases with the applied voltage. In the case of an exponential trap distribution, the energy distance of the Fermi-level from the valence band should be expressed by the relation;

$$E_f = k T_c \ln \left(\frac{(L+1)^2 e H_0 d^2}{L(2L+1) \epsilon \epsilon_0 V} \right) \dots \dots \dots (2)$$

The density of free carriers, which is proportional to the current, is given by the relation;

$$n_f = N_0 \exp (-E_f / kT) \dots \dots \dots (3)$$

Therefore, the temperature dependence of the SCL current yields E_f . Figure 5 shows the plot of the obtained activation energy versus the applied voltage. The experimentally obtained activation energy approximately agrees with the calculated value with equation (2), though an extreme case was assumed.

Thus, the above described electrolytic solutions form ohmic contacts with PVK films, and the injection of holes into PVK films can be achieved with these solutions. Also, the SCL hole current can be expressed by assuming an exponential trap distribution. These exponentially distributed traps would be mainly due to the structural disorder in amorphous PVK films.

References

- 1) M.A. Lampert and P. Mark, Current Injection in Solids, Academic Press, New York, (1970).
- 2) W. Helfrich, Physics and Chemistry of the Organic Solid State, Vol.3, edited by D. Fox, M.M. Labes and A. Weissberger, Interscience, New York, (1967) p.1.
- 3) M. Campos, Mol. Cryst. Liq. Cryst., 18, 105 (1972).
- 4) K. Okamoto, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, 46, 1948 (1973).
K. Okamoto, S. Kusabayashi, and H. Mikawa, ibid., 46, 1953 (1973).
- 5) J. Patora, J. Piotrowski, M. Kryszewski, and A. Szymański, Polymer Lett., 10, 23 (1972).
- 6) H. Kallmann and M. Pope, Rev. Sci. Instr., 30, 44 (1959).
- 7) Ag^{2+} solution: $10^{-3}M$ AgO was dissolved in 7.5N HNO_3 , NaI solution: 1N NaI aqueous solution was saturated with iodine, Ce^{4+} solution: $10^{-2}M$ $Ce(SO_4)_2$ was dissolved in 15N H_2SO_4 .
- 8) P.B. Ayscough and A.K. Roy, J. Polymer Sci., Part A-1, 6, 1307 (1968).
- 9) K. Tsuji, K. Takakura, M. Nishi, K. Hayashi, and S. Okamura, ibid., Part A-1, 4, 2028 (1966).
- 10) I. Gränacher, Solid. State. Comm., 2, 365 (1964)
- 11) P. Mark and W. Helfrich, J. Appl. Phys., 33, 205 (1962).
- 12) W.D. Gill, J. Appl. Phys., 43,5033 (1972).

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