

MEASUREMENT METHOD AND PHYSICAL MODEL OF VSC CONDUCTIVITY AND ITS APPLICATIONS IN CONDUCTING POLYMERS

WAN Meixiang (万梅香)

(*Institute of Chemistry · Academia Sinica · Beijing*)

ABSTRACT

Method of VSC (Voltage Shorted Compaction) can be used to determine the intrinsic temperature dependence of conductivity of polycrystalline compaction. The experimental conditions and technical key for preparation of VSC device and its physical model as well as its applications in conducting polymers are discussed in detail.

INTRODUCTION

The standard four probe method is used to measure the conductivity of single crystal of organic conductor and its temperature dependence of conductivity. Four probe method on pallet of polycrystalline powder, however, faces the problems of anisotropy in conductivity and interparticle contact resistance. The compaction conductivity obtained by four probe method, therefore, could not reflect the intrinsic properties of material when the temperature dependence of conductivity is measured. It means that the temperature dependence of conductivity of compaction often would be marked by that of interparticle contact resistance in compaction. Obviously, this is a very serious problem when the interparticle contact resistance is large. It will be understood more clear from the discussions on physical model of VSC method later. Only by measurement on single crystal, it can give us reliable conductivity of material. The growth of single crystal of organic conductor, however, is very difficult. It is, therefore, necessary to find a method to show qualitatively the temperature dependence of conductivity of newly synthesized organic conductor before the growing of single crystal. Fortunately, Coleman^[1] first suggested a VSC (Voltage Shorted Compaction) method in 1973 and showed that the temperature dependence of conductivity of TTF-TCNQ and NMP-TCNQ charge transfer complexes obtained from VSC method were in agreement with the results obtained from single crystal. In his introduction of VSC^[2], however, the experimental conditions and effects of preparation on VSC measurement had not been discussed. We have studied the VSC method in detail and demonstrated that the temperature dependence of conductivity of Qn (TCNQ)₂ obtained by VSC method was in agreement with the results obtained from its single crystal^[3]. Moreover, a very simple and useful physical model for VSC measurement was proposed^[4] and it was successfully applied to show the metallic temperature dependence of conductivity of highly doped polyacetylene^[5], polypyrrole^[6-7] and polythiophene^[8]. It is very interesting to find that some informations may be

obtained by VSC measurement which will not be observed by using standard four probe method due to differences in preparation method for conducting polymers .

In this paper , measuring method of VSC conductivity , experimental conditions and technical key for preparation of VSC device , physical model of VSC and its applications in conducting polymers were discussed in detail .

MEASURING METHOD OF VSC CONDUCTIVITY

The VSC method comes from four probe method . It is , however , different from four probe method as shown in Fig. 1 – a . As known to all , four probes with the same distance are used as electrical contact in four probe method . In this method , 1 and 4 terminals are used as current terminal , while , 2 and 3 terminals are used as voltage terminals . According to four probe method , a constant current passes through specimen from two current terminal by constant current sources , then the potential difference between two voltage terminals is measured by voltmeter . The main differences of VSC method from standard four probe method is that the specimen between two voltage terminals is coated by a very thin layer of silver paste as shown in Fig.1 – b . As a result , the interparticle contact resistance in VSC device was shorted by silver paste . That is why intrinsic temperature dependence of conductivity of organic conductor with intercrystalline could be showed by VSC method . It is suggested that the VSC method has a very important position in qualitative characterization of newly synthesized organic conductor before the growing of single crystal . Unfortunately , the specific conductivity of VSC device itself is not pyhsical meaning at all because of the conductivity of VSC device including the conductivity of silver paste .

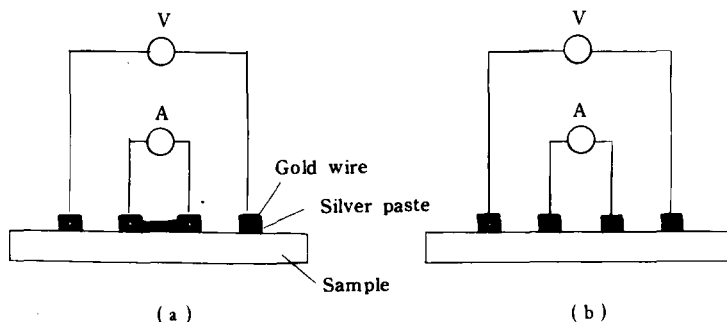


Fig.1 Structure of VSC device and four probe method for measurement of organic conductor
(a) VSC measurement ; (b) four probe method

PHYSICAL MODEL OF VSC MEASUREMENT

1. Physical model of series – parallel with three layers

The cross – section of the regions between two voltage terminals of the VSC device is shown in Fig.2. The VSC device consists of three layers . Layer A is silver paste itself and the resistance of this layer is that of silver paste itself . Layer B is considered to be material particles immersed in the silver paste because the particles of silver paste could be diffused into tested material by solvent . The interparticle contact resistance ,

therefore, are completely shorted by silver paste. The resistance of layer B, in fact, should be a very complex function of resistance of material and silver paste. In order to make simple and clear, the resistance of layer B could be considered as the resistance of material and silver paste in series. Similarly, layer C is the organic conductor itself and its resistance consists of resistance of material and interparticles contact resistance in series. The resistances between voltage terminal of VSC device, therefore, consists of the resistance of A, B and C layer in parallel. This is called physical model of series-parallel with three layers for VSC measurement and the mathematical expressions of conductivity and temperature dependence of conductivity for VSC device are shown as equation (1-3) respectively.

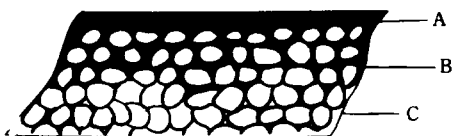


Fig.2 Schematic showing of the cross-section of the region between terminals 2, 3 of the VSC device.

A: conducting silver paste;

B: wetted layer;

C: organic conductor sample layer

$$\sigma_{\text{VSC}}(T) = A\sigma_A(T) + B \frac{\sigma_A(T) \cdot \sigma_s(T)}{\sigma_s(T)\varphi_A/\varphi_s + \sigma_A(T)} + C \frac{\sigma_C(T) \cdot \sigma_s(T)}{\sigma_C(T) \cdot \sigma_s(T)} \quad (1)$$

$$\begin{aligned} \frac{\partial}{\partial T} \sigma_{\text{VSC}}(T) = & \left[A + B \frac{\sigma_s(T)}{\sigma_A(T) + \varphi_A/\varphi_s \cdot \sigma_s(T)} \right] \frac{\partial}{\partial T} \sigma_A(T) \\ & + C \frac{\sigma_s(T)}{\sigma_s(T) + \sigma_C(T)} \frac{\partial}{\partial T} \sigma_s(T) \\ & + \left[B \frac{\sigma_A(T)}{\sigma_A(T) + \varphi_A/\varphi_s \cdot \sigma_s(T)} + C \frac{\sigma_C(T)}{\sigma_s(T) + \sigma_C(T)} \right] \\ & \cdot \frac{\partial}{\partial T} \sigma_s(T) \end{aligned} \quad (2)$$

and

$$A = \frac{d_1}{d_1 + d_0}, \quad B = \frac{d_2}{d_1 + d_0} \cdot \frac{1}{\varphi_s}, \quad C = \frac{d_0 - d_2}{d_1 + d_0}$$

where σ_{VSC} , σ_A and σ_s is the conductivity of VSC device, silver paste and organic conductors respectively; σ_c is contact conductivity of interparticle in organic conductors. φ_A and φ_s is the volume fraction of silver paste and organic conductor in wetted layer B respectively. As shown in equation (1) and (2), it indicates that the conductivity of VSC device has very complex function depending the conductivity of silver paste and organic conductor as well as contact conductivity of interparticles. It is, therefore, difficult to show the physical meaning from equation (1) and (2) for VSC measurement.

For VSC device, in fact, the conductivity of silver paste is the largest, while, the contact conductivity of interparticle is the lowest. So, a specific condition of $\sigma_A(T) \gg \sigma_s(T) \gg \sigma_c(T)$ and $\varphi_A \ll \varphi_s$ are satisfied. At these conditions, therefore, the VSC conductivity can be expressed by equation (3) and (4).

$$\sigma_{\text{VSC}}(T) \doteq A\sigma_A(T) + B\sigma_s(T) + C\sigma_c(T) \quad (3)$$

$$\frac{\partial}{\partial T} \sigma_{\text{VSC}}(T) = A \frac{\partial}{\partial T} \sigma_A(T) + B \frac{\partial}{\partial T} \sigma_s(T) + C \frac{\partial}{\partial T} \sigma_c(T) \quad (4)$$

It indicates that the VSC conductivity are the sum of that of silver paste , organic conductor and interparticle contact . Similarly , the behavior of temperature dependence of VSC conductivity depends on the characteristic of temperature dependence of silver paste , organic conductor and interparticle contact . In order to understand the physical meaning of VSC model , some of specific conditions are going to discuss in detail as follows :

$$(1) d_1 = d_2 = 0$$

Under above condition , it means the VSC device is without layer of silver paste , the equation (3) and (4) would be expressed by equation (5) and (6)

$$\sigma_{\text{VSC}}(T) = \sigma_{F \cdot P}(T) = C \frac{\sigma_c(T) \cdot \sigma_s(T)}{\sigma_c(T) + \sigma_s(T)} \quad (5)$$

$$\begin{aligned} \frac{\partial}{\partial T} \sigma_{\text{VSC}}(T) &= \frac{\partial}{\partial T} \sigma_{F \cdot P}(T) = \frac{\sigma_s^2(T)}{[\sigma_s(T) + \sigma_c(T)]^2} \cdot \frac{\partial}{\partial T} \sigma_c(T) \\ &+ \frac{\sigma_c^2(T)}{[\sigma_s(T) + \sigma_c(T)]^2} \cdot \frac{\partial}{\partial T} \sigma_s(T) \quad (6) \end{aligned}$$

It is very clear to show that the VSC measurement was reduced into standard four probe method . It indicates that the temperature dependence of conductivity of compaction obtained by four probe method could not reflect its intrinsic behavior of temperature dependence of conductivity due to existence of the contact resistance of interparticle in compaction . If $\sigma_s(T) \gg \sigma_c(T)$ the equation (5) and (6) might be written by

$$\sigma_{\text{VSC}}(T) = \sigma_{F \cdot P}(T) = C \sigma_c(T) \quad (7)$$

$$\frac{\partial}{\partial T} \sigma_{\text{VSC}}(T) = \frac{\partial}{\partial T} \sigma_{F \cdot P}(T) = C \frac{\partial}{\partial T} \sigma_c(T) \quad (8)$$

It is suggested that the temperature dependence of conductivity of intercrystalline compaction obtained by four probe method are fully marked by that of interparticle contact resistance . This is why the temperature dependence of conductivity of intercrystalline compaction obtained by four probe method can not reflect the intrinsic properties of material when the resistance of interparticle contact is much large.

$$(2) d_2 = 0 \text{ but } d_1 \neq 0 \text{ and } \sigma_A(T) \gg \sigma_c(T)$$

At this condition , the equation (3) and (4) might be written as

$$\sigma_{\text{VSC}}(T) = A \sigma_A(T) \quad (9)$$

$$\frac{\partial}{\partial T} \sigma_{\text{VSC}}(T) = A \frac{\partial}{\partial T} \sigma_A(T) \quad (10)$$

This shows that the behavior of temperature dependence of conductivity of VSC device would be the same as that of silver paste when the VSC device without wetted

layer B. It means that all current applied will pass through silver paste layer as the VSC device without wetted layer B. Formation of wetted layer B, therefore, is the technical key to make the VSC device and to obtain successful results for VSC measurement.

2. Physical model of series-parallel with two layers

In general, the contact resistance of interparticle are the largest, while the resistance of silver paste is the lowest in practical VSC device. As a result, the conditions of $\sigma_A(T) \gg \sigma_S(T) \gg \sigma_C(T)$ and $\varphi_A \ll \varphi_S$ are satisfied. Therefore, the main current will pass through the layer A and B according to the principle of divert. It is suggested that only the current path of layer A and B considered could show a good approximation. The mathematical expressions of VSC conductivity based on physical model with two layers are written as the equations

$$\sigma_{\text{VSC}}(T, E) = A\sigma_A(T, E) + B\sigma_S(T, E) \quad (11)$$

$$\frac{\partial}{\partial T} \sigma_{\text{VSC}}(T, E) = A \frac{\partial}{\partial T} \sigma_A(T, E) + B \frac{\partial}{\partial T} \sigma_S(T, E) \quad (12)$$

$$\frac{\partial}{\partial E} \sigma_{\text{VSC}}(T, E) = A \frac{\partial}{\partial E} \sigma_A(T, E) + B \frac{\partial}{\partial E} \sigma_S(T, E) \quad (13)$$

Since the metallic temperature dependence of conductivity of silver paste has been demonstrated by experiments^[3], so the temperature dependence of conductivity of VSC device is determined by that of material tested. That is why VSC method is able to stimulate the temperature dependence of conductivity of single crystal as shown as equation (12). Similarly, according to equation (13), one can see that the field dependence of conductivity for VSC measurement is also controlled by that of material

tested because of metal character of silver paste $\left(\frac{\partial}{\partial E} \sigma_A(T, E) = 0 \right)$.

CHARACTERISTICS OF CONDUCTIVITY-TEMPERATURE FOR VSC MEASUREMENT AND ITS PHYSICAL MEANING

In general, for measurement of organic conductor, the temperature dependence of conductivity usually shows as $\sigma(T)/\sigma_{RT}$. Therefore, the equation (11) and (12) could be expressed by equation (14) and (15) as

$$\beta_{\text{VSC}}(T) = A' \beta_A(T) + B' \beta_S(T) \quad (14)$$

$$\frac{\partial}{\partial T} \beta_{\text{VSC}}(T) = A' \frac{\partial}{\partial T} \beta_A(T) + B' \frac{\partial}{\partial T} \beta_S(T) \quad (15)$$

$$A' = A \cdot \frac{\sigma_A(RT)}{\sigma_{\text{VSC}}(RT)}; \quad B' = B \cdot \frac{\sigma_S(RT)}{\sigma_{\text{VSC}}(RT)}$$

$$A = \frac{d_1}{d_1 + d_0}, \quad B = \frac{d_2}{d_1 + d_0} \cdot \frac{1}{\varphi_S} \quad (16-a)$$

and

$$\beta_{\text{VSC}}(T) = \frac{\sigma_{\text{VSC}}(T)}{\sigma_{\text{VSC}}(RT)} \quad (16-b)$$

$$\beta_A(T) = \frac{\sigma_A(T)}{\sigma_A(RT)}$$

$$\beta_S(T) = \frac{\sigma_S(T)}{\sigma_S(RT)}$$

In experiment, four kinds of $\beta_{VSC}(T) \sim T$ curve are observed as shown in Fig. 3. Based on the location of $\beta_{VSC}(T) \sim T$ curve comparison with curve of silver paste, the character of temperature dependence of conductivity for tested material is able to be known as the following:

(1) Silver paste itself

The temperature dependence of conductivity of silver paste can be measured from experiment^[3] and its characteristic of conductivity – temperature is shown in Fig.(3-B). If the curve of $\beta_{VSC}(T) \sim T$ is the same as B curve, it indicates that the VSC measurement is not successful due to all of current being passed through the silver paste. For this situation, it is necessary to measure again by changing shorted resistance of VSC device.

(2) Metallic Type

The characteristic of temperature dependence of conductivity for metallic material is that its conductivity increases with the decrease of temperature, i.e., $\frac{\partial}{\partial T} \sigma(T) < 0$. So, the temperature

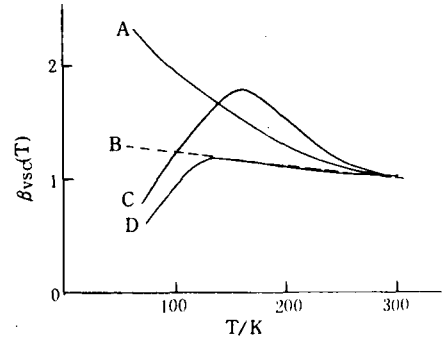


Fig. 3 Characteristic of temperature dependence of conductivity obtained by VSC measurement

- A metallic type;
- B conducting silver paste;
- C semiconductor type;
- D transition of metal-semiconductor.

dependence of conductivity of material tested should be metallic character if the $\beta_{VSC}(T) \sim T$ curve is located above the curve of silver paste and $\frac{\partial}{\partial T} \beta_{VSC}(T) < 0$ as shown in Fig.(3-A). It is demonstrated that the condition of $\frac{\partial}{\partial T} \beta_{VSC}(T) < 0$ must

be required if the condition of was satisfied due to $|\frac{\partial}{\partial T} \beta_{VSC}(T)| > |\frac{\partial}{\partial T} \beta_A(T)|$ and

$$\frac{\partial}{\partial T} \beta_A(T) < 0.$$

(3) Semiconductor type

The temperature dependence of conductivity of semiconductor shows that its conductivity increases with increasing temperature, i.e., $\frac{\partial}{\partial T} \sigma(T) > 0$. Similarly, the temperature dependence of conductivity of material tested shows semiconductor character if the $\beta_{VSC}(T) \sim T$ curve is located below the curve of silver paste and $\frac{\partial}{\partial T} \beta_{VSC}(T) > 0$ as shown in Fig.(3-C). It suggested that $\frac{\partial}{\partial T} \beta_S(T) > 0$ is satisfied when

$\frac{\partial}{\partial T} \beta_s(T)$ is positive due to $\frac{\partial}{\partial T} \beta_{vsc}(T) < 0$ and $|\frac{\partial}{\partial T} \beta_{vsc}(T)| < |\frac{\partial}{\partial T} \beta_A(T)|$

(4) Transition of metal – semiconductor

In experiment, a maximum of conductivity at $T = T_c$ for VSC measurement is also observed as shown in Fig. (3–D). It suggested that the tested material showed a metallic behavior at $T > T_c$, while, a semiconductor character was observed at $T < T_c$. Currently, it is very hard to say that if it has the same meaning of transition of metal – semiconductor. It should be noted that the magnitude of maximum conductivity in VSC measurement depends on the shorted resistance of VSC device, on the other hand, the position of peak in VSC measurement shows the intrinsic character of tested material.

APPLICATIONS OF VSC MEASUREMENT IN CONDUCTING POLYMERS

Doped polyacetylene created by MacDiarmid^[9] is the first example as conducting polymers and metal – like character has been revealed from their optical properties^[10], thermoelectric power^[11] and magnetic susceptibility measurements^[12]. The metallic temperature dependence of its conductivity, however, is not observed by standard four

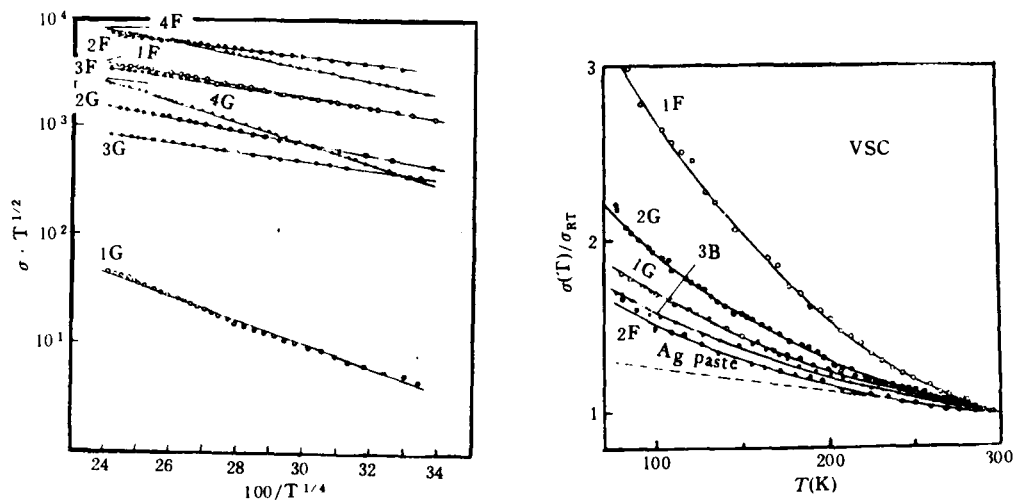


Fig.4 Temperature dependence of the conductivity of doped polyacetylene films

dopant : 1, 2, 3 and 4 is ClSO_3H , $\text{NaClO}_4 \cdot \text{I}_2$.

F : fibrillar morphology ; G : granular morphology .

(a) : obtained by standard four probe method ; (b) : obtained by VSC measurement .

probe method and a thermally activated conduction characteristic as semiconductor has been observed (Fig. 4 – a). This has been interpreted by Mott model of variable range hopping among localized states near fermi surface^[13]. This is not true temperature dependence of conductivity intrinsics of the interfibrillar or intergranular contacts. In fact, many compressed parallels of polycrystalline molecular solids^[14] and copper phthalocyanine evaporated film^[15] also show such temperature dependence of their conductivity. That is, therefore, attributed to the contact resistance in the interfibrillar of film because of the fibrillar morphology of polyacetylene film obtained by

polymerization. This situation is similar to the compaction with intercrystalline. Therefore, VSC method can be used to eliminate the contact resistance of interfibrillar or intergranular in film of conducting polymers to show its intrinsic behavior. We used successfully VSC method to determine the metallic temperature dependence of conductivity of highly doped polyacetylene^[5] (See Fig. 4-b); polypyrrole^[6-7] (See Fig. 5) and polythiophene^[8]. It should be noted that some informations might be obtained by VSC measurement which is not observed using standard four probe method. For example, the differences in behavior of temperature dependence of conductivity of doped polythiophene obtained by electrochemically and chemically polymerization were observed by VSC measurement as shown in Fig. 6. It is very clear to show that a metal-like character for chemically oxidized doped polythiophene has been observed, while, a broad maximum at about 100 K for electrochemically prepared doped polythiophene

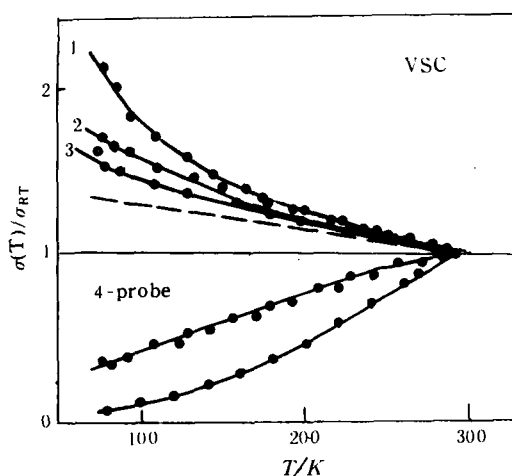


Fig.5 Temperature dependence of the conductivity of doped polypyrrole films obtained by standard four probe method and VSC measurement.

Counter ions: (1) BF_4^- ; (2) ClO_4^- ; (3) HSO_4^- , --- : conducting silver paste.

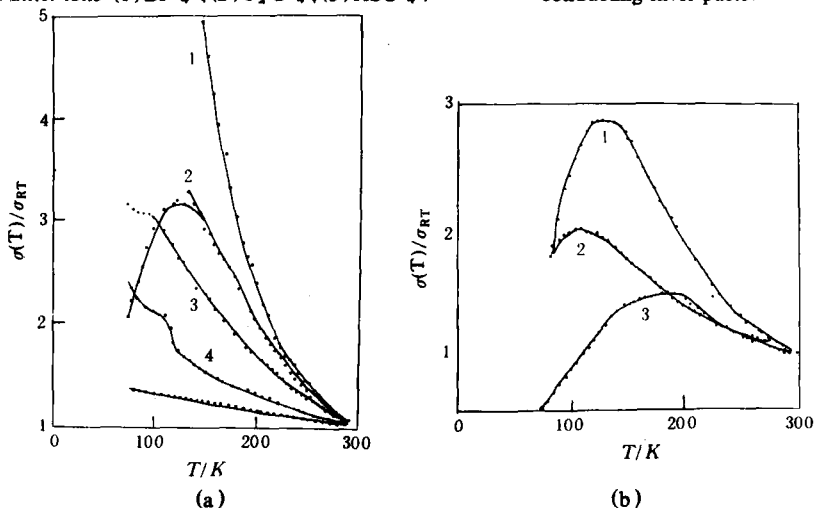


Fig.6 Temperature dependence of the conductivity of doped polythiophene films

(1) $(\text{C}_4\text{H}_2\text{S})(\text{FeCl}_3)_{0.15}$; (2) $(\text{C}_4\text{H}_2\text{S})(\text{PF}_6)_{0.34}$; (3) $(\text{C}_4\text{H}_2\text{S})(\text{SbF}_6)_{0.15}$; (4) $(\text{C}_4\text{H}_2\text{S})(\text{ClO}_4)_{0.26}$; (5) --- silver paste
(a) chemically polymerization; (b) electrochemically polymerization.

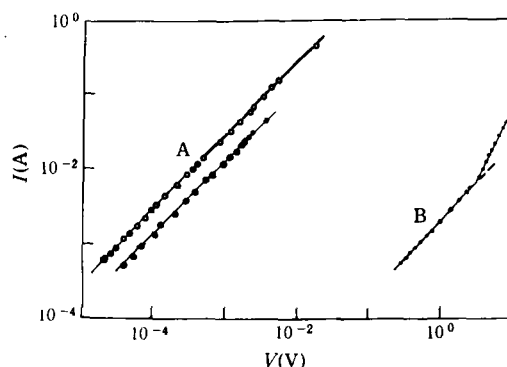


Fig.7 Non-Ohmic conductivity of doped polythiophene films with SbF_6^- ions
A obtained by VSC measurement ; B obtained by four probe method .

has been obtained . Moreover , VSC measurement has been used to show the intrinsic electrical field dependence of conductivity for doped polythiophene . A non-Ohmic characteristic of highly doped polythiophene by standard four probe method . This non-Ohmic characteristic is due to contact effect of intergranular or interfibrillar morphology in film of conducting polymers . On the other hand , an Ohmic conductivity was observed by VSC measurement as shown in Fig. 7. Moreover , Masubuchi et al .^[17] demonstrated that the metallic temperature dependence of conductivity in doped polyacetylene films was observed by VSC measurements . The results of VSC measurements were interpreted by the interfibrillar resistance of highly doped polyacetylene was metallic and obeyed a T^2 law through the whole temperature range 1.9 — 300 K . Recently , the author has observed a maximum conductivity of protonated polyaniline at about 130 K by VSC measurement .

CONCLUSION

1. In experiments , VSC method was demonstrated that it could be used to determine qualitatively the intrinsic properties of temperature dependence of conductivity of tested material due to eliminate the intercrystalline contact resistance by means of coating a thin layer of silver paste . On the other hand , the specific conductivity of VSC device itself has not any physical meaning due to existence of conductivity of silver paste in VSC device .

2. A physical model of VSC measurement proposed by the author is able to interpret why that the VSC method could be used to determine the intrinsic behavior of conductivity — temperature of tested material .

3. According to mathematical analysis of physical model of VSC method , the wetted layer B is a technical key for preparation of VSC device . It should note that the thickness of silver paste should be thinner as possible in order to have successful VSC measurement .

4. The VSC method can be used to show the intrinsic character of temperature dependence of conductivity of conducting polymers .

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