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The Thermal Stability of Metal Cation-TCNQ Anion Radical Salts

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To study the thermal stability of several metal cation–TCNQ salts (mainly alkali metal salts), the variation in the electrical resistivity and the characteristics of the chemical degradations by heating were measured. Most metal–TNCQ salts do not melt and are not sublimated, but have decomposition points at about 320 °C. Na(TCNQ) has a stable resistivity, even after heating for 500 hours at 200 °C, and is the most stable among the metal–TCNQ salts tested. Metal–TCNQ salts are gradually damaged from the surfaces of the crystalline powders by heating, and the TCNQ molecule is oxidized, thus losing CN groups. The crystallization process of the TCNQ salts has a great influence upon their thermal stabilities. In the complex salt $Cs_2(TCNQ)_3$, the application of d.c. voltage gives rise to the polarization current at a temperature near 200 °C, and the TCNQ molecules tend to migrate in the electric field.

Charge-transfer complexes based on 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been extensively studied as organic metals or one-dimensional conductors in recent years; they have also received considerable interest in connection with their possible use as electronic materials.[1,2] Considering the life as electronic material or the compounding process with polymeric materials in practical use, the thermal stability of a TCNQ complex is highly important. Many TCNQ complexes with organic electron-donors are susceptible to thermal decomposition; metal–TCNQ salts are thermally more stable because of the low ionization potentials of metals. However, the thermal stability of the metal–TCNQ salts has been studied only by DTA and TGA.[3,4]

In this paper, in order to ascertain the upper limit of the thermal stability of TCNQ complexes, the thermal stabilities of several metal cation–TCNQ anion radical salts (mainly alkali metal salts) have been studied from both sides of their electrical resistivities and chemical degradations. The thermal stabilities have mainly been studied at the comparatively high temperatures of 200—250 °C in air; after the heating at 200—250 °C, the resistivity and chemical degradation of the TCNQ salts were measured at room temperature (RT). To study the variation in the resistivity, the dependence of the RT resistivity on the heating time, the temperature dependence of the resistivity, the d.c. polarization currents at temperatures ranging from RT to 200 °C, and the differences in the variation in the resistivity with several crystallization methods were measured. Moreover, the chemical degradations were analyzed by means of DTA, TGA, IR spectra, elemental analysis, or X-ray powder diffraction patterns.

Experimental

Synthesis of Metal-TCNQ Salts. Polycrystalline samples of Li(TCNQ), Na(TCNQ), K(TCNQ), $Cs_2(TCNQ)_3$, $Ba(TCNQ)_2$, and Cu(TCNQ) were prepared by refluxing for 4 h mixed acetonitrile solutions of TCNQ and metal iodides.[3] CsI and $BaI_2\cdot 2H_2O$, which are insoluble in acetonitrile, were dissolved in a small amount of methanol, after which the solutions were added to TCNQ solutions. The hot mixed solutions were cooled to 0 °C, and the polycrystalline powders of the TCNQ salts thus deposited were filtered off and washed with acetonitrile.

Electrical Measurements. About constant weights of the polycrystalline powder samples were introduced into glass capillaries 1.5 mm in inner diameter and were packed to a saturated thickness of about 1 mm by pressing them repeatedly (about thirty times) under a weight of 230 g. Under a pressure of 13 kg/cm^2 and using electrodes composed of stainless steel sticks, the resistances for d. c. voltage were measured. In order to check the correctness of electrical measurements, the following measurements were carried out. The resistance was influenced by the pressure and electrode materials, but was over the wide range of 0.3—300 V/cm and showed a linear dependence on the thicknesses of the samples in the capillaries. When graphite powders were used as elctrodes instead of stainless steel, the samples showed lower resistivities, but the temperature dependence of their resistivities had the same temperature coefficients. Further, both these samples showed constant currents for 1 h under a voltage of 10 V at 30, 45, 60, 80, and 100 °C.

Analysis of Degradated Products. The IR spectra were measured by means of a JASCO Model DS-403G infrared spectrophotometer using the KBr-wafer technique. The DTA and TGA were performed by using an electric microbalance(Rigaku Electric Co., Ltd.), and each sample was measured under the following two conditions: by increasing the temperature at the rate of 10 °C/min from RT to 1000 °C, or by holding the temperature at 250 °C for 1 h after increasing temperature at the rate of 2.5 °C/min from 200 °C to 250 °C. The X-ray diffraction patterns were measured by means of a Philips PW-1009 X-ray diffractometer, using Cu $K\alpha$ radiation as the X-ray source(35 kV, 10 mA).

Results and Discussion

Thermal Stability of Resistivity. The temperature dependences of the resistivity of metal–TCNQ salts are shown in Fig. 1. All these curves except that of K(TCNQ) are in accord with Arrhenius' equation at temperatures below 120 °C, but crystals of K(TCNQ) show unstable non-linear characteristics. The time dependence of the resistivity at 200 °C under a d.c. voltage of 10 V (about 100 V/cm) is shown in Fig. 2; $Cs_2(TCNQ)_3$ shows a remarkable variation in the current based on the polarization of the carriers. The variation in the resistivities with the time at 200 °C is faster, probably because of the existence of the electric field, than that (Fig. 3(1)) of the salts loaded only with heat at 200 °C. The resistivities of metal–TCNQ salts cooled from 200 °C to RT become higher than those shown in Fig. 1 as well as in Ref. 5, but the

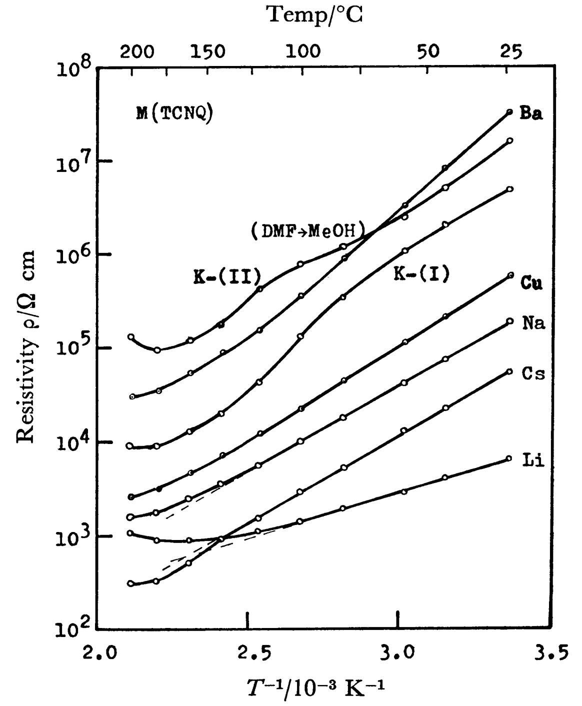

Fig. 1. Temperature dependence of resistivity of metal–TCNQ salts.

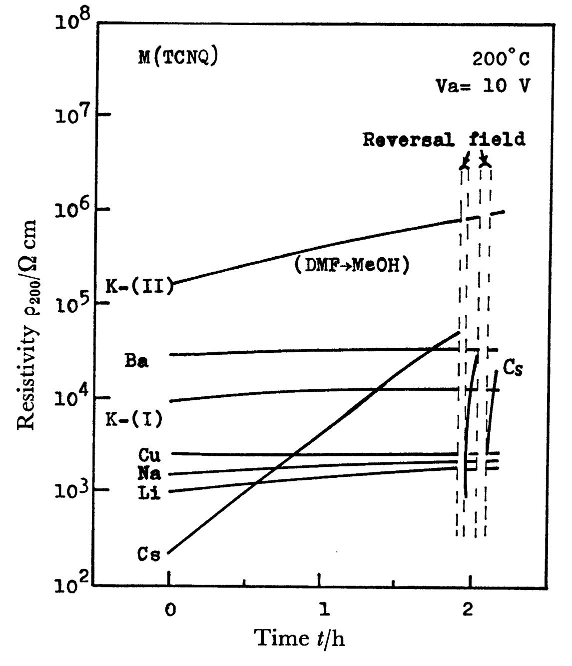

Fig. 2. Dependence of resistivity on time at 200 °C under d.c. voltage of 10 V (about 100 V/cm).

variations in the resistivities of Na(TCNQ), Cu(TCNQ), and Ba(TCNQ)$_2$ were only small.

After the six kinds of metal–TCNQ salts were heated at 200, 220, and 250 °C, their resistivities were measured at the RT of 24 °C. The results are shown in Fig. 3 and Table 1. Here, Li(TCNQ)-A and Na(TCNQ)-A are new samples synthesized at the same time as the other metal salts, while Li(TCNQ)-B and Na(TCNQ)-B are old samples synthesized about 9 years ago and kept

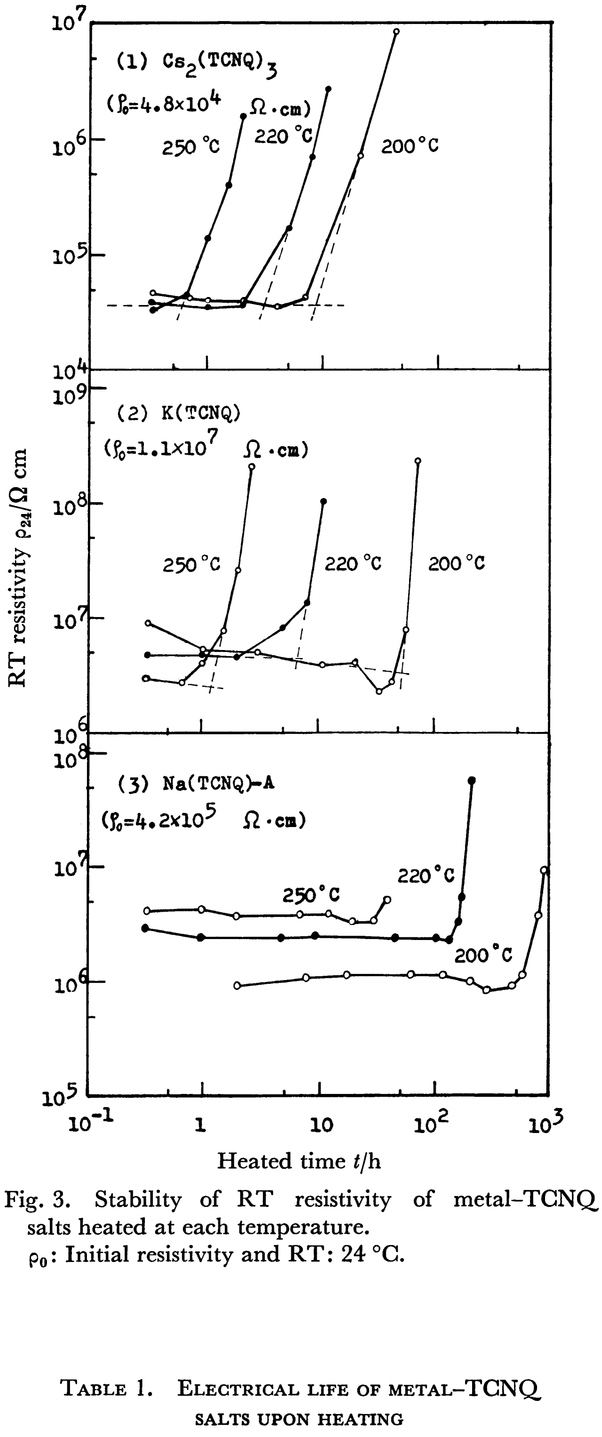

Fig. 3. Stability of RT resistivity of metal–TCNQ salts heated at each temperature.
ρ_0: Initial resistivity and RT: 24 °C.

Table 1. Electrical life of metal–TCNQ salts upon heating

Metal–TCNQ salt	Electrical life, t_{th}/h 250 °C	220 °C	200 °C
Li(TCNQ)-A[a]	—	—	64
Li(TCNQ)-B[b]	(1.2)	(6.3)	(15)
Na(TCNQ)-A	35	170	600
Na(TCNQ)-B	(11)	(72)	(175)
K(TCNQ)	1.25	6.8	55
Cs$_2$(TCNQ)$_3$	0.6	3	9
Ba(TCNQ)$_2$	2.3	8	24
Cu(TCNQ)	2	9	24

a) A: New sample. b) B: Sample synthesized 9 years ago.

in air for that long period. These results are characterized by the retention of comparatively constant resistivities, followed by rapid increases in the resistivities, with a resemblance to the induction period of thermal degradation in the stabilizer-filled polymer.6) Here, the threshold times at the variation points in these figures are evaluated from the intersecting points of the dashed lines and are here termed the "electrical life," t_{th}. The values of t_{th} are tabulated in Table 1. Na(TCNQ) has the longest life among the metal–TCNQ salts tested. These values of t_{th} belong to a very stable class of organic materials, and so the tested metal–TCNQ salts have been shown to have a satisfactory stability in practical use as electronic materials.

The t_{th}-1/T plots of K(TCNQ) shows straight lines, but the life at RT estimated from the linear characteristics of K(TCNQ) is too long. The t_{th}-1/T values of other metal–TCNQ salts, plotted from the data shown in Table 1, do not show straight lines, but the slopes of the plots are almost all the same. In order to estimate the life at RT, the t_{th}-1/T characteristics need to be measured over a range of temperatures wider than 200—250 °C. In Fig. 3, except for the case of $Cs_2(TCNQ)_3$, the value of ρ_{24} of each sample, which was heated at the temperatures of 200, 220, and 250 °C, varies even though the material is the same, but the results seem to be based on the change in the crystal state by heating at a different temperature or on the stresses of the crystal at the time of the drop in the temperature.

Thermal Degradation of Complex Salt – $Cs_2(TCNQ)_3$. $Cs_2(TCNQ)_3$ shows a remarkable variation in the current at temperatures near 200 °C, as is shown in Fig. 2, although the results of the elemental analysis of a sample heated for only 7.2 h at 200 °C show the same composition as virgin $Cs_2(TCNQ)_3$. Also after the reversal of the electric field, a remarkable variation in the current, the so-called absorption current, also occurs. Such characteristics are examples of ionic behavior based on the polarization of the carrier by an electric field, different from the constant current under a d.c. electric field in the case of electronic conduction, and show that TCNQ molecules in crystal of $Cs_2(TCNQ)_3$ easily migrate at temperatures close to 200 °C in response to the electric field. These factors coincide with the behavior shown in Ref. 7. Besides, needle crystals of $Cs_2(TCNQ)_3$ are gradually pulverized to microcrystals with the sublimation of a liberated molecule such as $TCNQ^0$ during the heating of 200—250 °C. The X-ray diffraction peaks of the heated $Cs_2(TCNQ)_3$ are also gradually lowered, while keeping the same peak pattern. Therefore, the thermal degradation of the salt is surmised to occur gradually from the surface of the crystal powders. After a longer heating, the composition of the degradated product seems to come close to the value of Cs(TCNQ) judging from the composition of elements shown in Table 2.

Thermal Degradation of Simple Salts. As is shown in Table 3, the DTA data indicate that the decomposition points are above 285 °C and that heating for 1 h at 250 °C does not cause any peak in the DTA curve. The weight losses also occur to only a small extent in that condition. However, upon heating for several hours at that temperature (250 °C), a rapid increment of resistivity occurs except in the case of Na(TCNQ), as is shown in Fig. 3 and Table 1. Na(TCNQ), whose electrical life, t_{th}, is 600 h at 200 °C has a very excellent stability. The high stability of Na(TCNQ) is considered to be related to the finding that the beginning temperature, T_{h2}, of the second peak in the DTA data is higher than that of the other salts by about 100 degrees. This high stability is probably due to the pertinence of the ionic radius of sodium, which has a low ionization potential in the crystal.

Many of these alkali or alkali earth metal–TCNQ salts whose metals have low ionization potentials are

TABLE 2. ELEMENTAL ANALYSIS, WEIGHT LOSS, AND SOLUBILITY OF METAL–TCNQ SALTS HEATED AT 200 °C

Sample a)		Color	Elemental analysis b)			Oxygen c) content	Weight loss	Solubility (Color of solution) d)	
			C/%	H/%	N/%	%	%	CH_3CN	H_2O
K(TCNQ)-I	0 h	deep red	59.56 (59.23)	1.48 (1.65)	23.45 (23.04)	0	0	△ (green)	×
	35 h	deep red	59.01	1.72	23.32	0	2.0	—	—
	71.5 h	black	56.65	1.76	20.76	3.59	6.7	—	—
	235 h	amber	48.22	2.08	11.92	18.3	17.3	—	—
K(TCNQ)-II	0 h	deep red	59.18 (59.23)	1.76 (1.65)	23.01 (23.04)	0	0	△ (green)	×
	4 h	deep red	56.77	1.74	20.88	4.87	2.8	—	—
	11.5 h	black	50.77	2.11	14.68	15.0	7.8	△ (light green)	△ (yellow)
	22 h	dark green	48.36	2.16	11.90	19.2	12.4	—	—
	40 h	amber	46.87	2.36	9.56	21.9	17.6	×	○ (amber)
	112.5 h	amber	45.26	2.35	8.96	23.1	20.8	×	○ (amber)
$Cs_2(TCNQ)_3$	0 h	purple	49.32 (49.21)	1.20 (1.37)	18.92 (19.14)	0	0	△ (light green)	×
	7.2 h	purple	49.52	1.30	19.38	0	0.6	—	—
	42 h	dark purple	44.14	1.48	14.95	6.03	9.4	×	○ (amber)
Na(TCNQ)-B	345 h	black	54.06	2.08	11.2	—	—	△ (light green)	△ (light green)

a) Time(h) is the heating time of the sample at 200 °C. b) Calculated value in parentheses. c) Value calculated from elemental analysis and weight loss. d) ○: Easily soluble, △: slightly soluble, and × : insoluble.

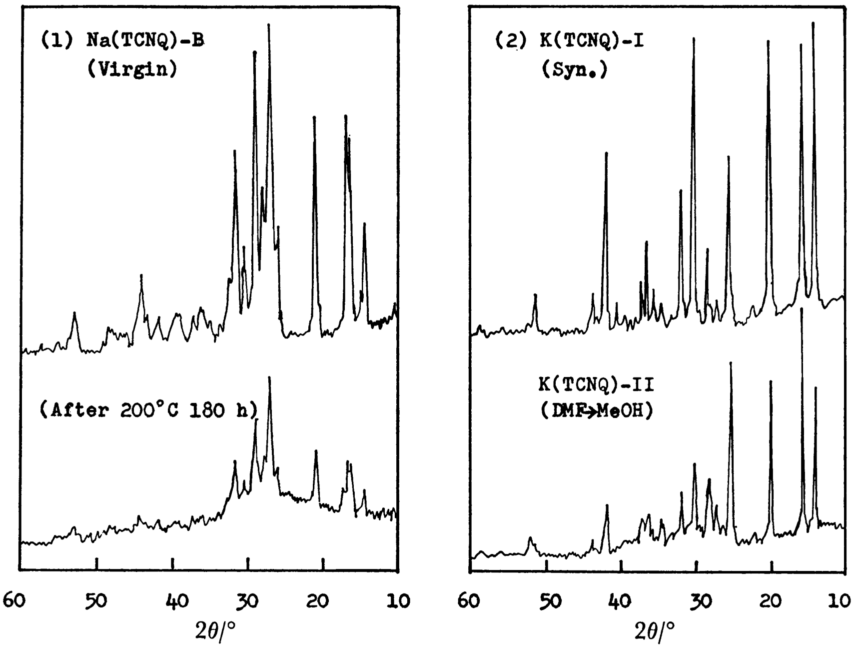

Fig. 4. Variation of X-ray diffraction patterns of Na(TCNQ) and K(TCNQ).

degradated to become black without any evaporation or sublimation, but K(TCNQ) changes its color variously with the degree of degradation, as will be shown below. Cu(TCNQ) sublimes near 355 °C, and its thermally decomposed product upon long heating at 200 °C seems to include metallic copper. This is probably due to the weak ionization tendency of copper. The results of elemental analysis are shown in Table 2. The metal–TCNQ salts are degradated to lose CN groups. In numerous cases of color changes of salts occurring with degradation, the degradation is characterized by a variation in the resistivity immediately after the color change. It is clear that the color change reflects the variation in the composition of TCNQ salt.

The X-ray diffraction peaks of Na(TCNQ) are lowered with its degradation, showing the same patterns as are shown in Fig. 4(1). Therefore, the thermal degradation is considered to occur gradually from the surface of the crystalline powders. Besides, the data of IR spectrophotometry on the degradated products of Na(TCNQ) and K(TCNQ) show peaks at the wave numbers of 750, 1380, 1670, 1740, and 3400 cm^{-1}. These peaks are deduced to show a hydrogen bond, carbonyl group, or carboxyl group formed by the oxidation of the TCNQ molecule, but the correct molecular structures of the degradated products of TCNQ salts are still not clear. The solubilities of the tested metal–TCNQ salts and their degradated products in water and in acetonitrile are tabulated in Table 2, along with the colors of the solutions. K(TCNQ) and $Cs_2(TCNQ)_3$ change to very water-soluble substances upon heating.

Thermal Stabilities of Various K(TCNQ) Crystals. K(TCNQ)-I was synthesized in acetonitrile by using the above-described method. By means of the recrystallization or reprecipitation of the K(TCNQ)-I, the following four kinds of K(TCNQ) were prepared:

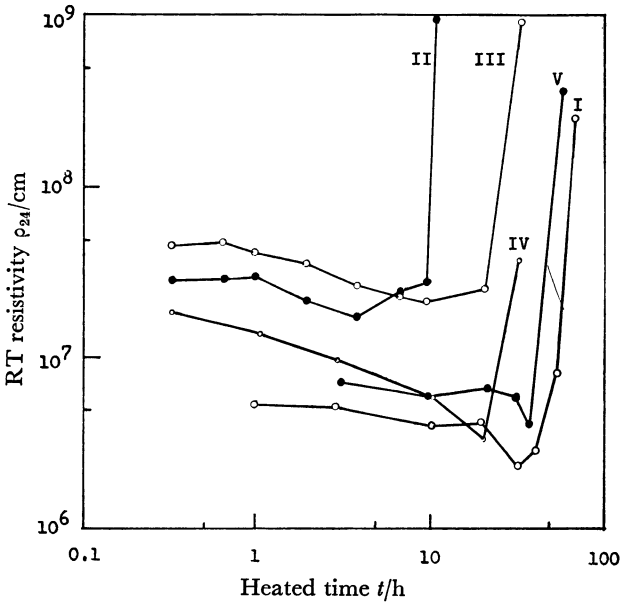

Fig. 5. Stability of RT resistivity of various K(TCNQ) crystals heated at 200 °C.
ρ_0: Initial resistivity and RT: 24 °C.
ρ_0/Ωcm: I 1.1×10^7, II 2.9×10^7, III 4.3×10^7, IV 2.8×10^7, V 6.2×10^7.

K(TCNQ)-II. . . . reprecipitated from a DMF solution of K(TCNQ)-I of 100 °C by dilution with much methanol at 0 °C.

K(TCNQ)-III. . . . recrystallized from a DMF solution of K(TCNQ)-I.

K(TCNQ)-IV. . . . once recrystallized from an acetonitrile solution of K(TCNQ)-I.

K(TCNQ)-V. . . . twice recrystallized from an acetonitrile solution of K(TCNQ)-I.

These crystals of K(TCNQ) have the virgin resistivities, ρ_0, shown in Fig. 5, but it is strange that their

Table 3. Thermal analysis of metal–TCNQ salts by DTA and TGA

	T_h/°C			Weight loss/%[a)]			Residue at 1000 °C/%	Weight loss/%[b)]	
	T_{h1}	T_{h2}	T_{h3}	T_w	$T_w \to T_{h2}$	$T_{h2} \to 1000$ °C		Before 250 °C	After 250 °C 1 h
K(TCNQ)-I	315	450	630	310	9.5	71	19.5	0	1.0
K(TCNQ)-II	285	450	590	275	14	66.5	19.5	0	14.2
K(TCNQ)-IV	310	450	660	300	10	74.5	15.5	0	8.0
K(TCNQ)-V	320	450	680	315	9.5	78	22.5	0	4.0
Na(TCNQ)-B	340	545	660	330	18.5	60.5	21	0	2.6
Li(TCNQ)-B	325	430	475	315	19	62.5	18.5	2	3.5
$Cs_2(TCNQ)_3$	320	455	—	310	11.5	61.5	27	0	3.5
Cu(TCNQ)	355			355	80	—	20	0	0.3
$Ba(TCNQ)_2$	370	430	—	355	23.5	46.5	30	0	0.5

T_h and T_w are the beginning temperatures of the exothermic peak and the weight loss respectively. a) 10 °C/min from RT to 1000 °C. b) 2.5 °C/min from 200 °C to 250 °C and hold at 250 °C for 1 h.

resistivites are about one order of magnitude higher than the values measured immediately after compacting the crystalline powders into a capillary. The variation in the RT resistivities of these K(TCNQ) crystals upon heating at 200 °C is also shown in Fig. 5. K(TCNQ)-II shows the most unstable result among the samples (I—V) in the figure; the results have a tendency similar to that of the DTA data shown in Table 3. Since the K(TCNQ)-II does not show any weight loss at temperatures below 250 °C, but does show low peaks in the X-ray powder pattern, as is shown in Fig. 4(2), this instability may be deduced to be based on the difference is crystal states rather than a residual DMF solvent.

Figure 5 shows that the crystallization processes exert great influences upon their thermal stabilities; it is interesting that K(TCNQ)-I, prepared in synthesis, shows a fairly stable result. In the heating process, K(TCNQ) crystals show various color changes different from those of many metal–TCNQ salts, as is shown in Table 2; the color changes of K(TCNQ)-(I—V) correspond to the variation in resistivities shown in Fig. 5.

In conclusion, the thermal stabilities of metal–TCNQ salts may be summarized as follows:

(1) Na(TCNQ) has a stable resistivity, even after heating for 500 h at 200 °C, and is the most stable among the metal–TCNQ salts tested.

(2) Most of the metal–TCNQ salts do not melt and are not sublimated, but have a decomposition point at about 320 °C.

(3) Metal–TCNQ salts are considered to be gradually damaged from the surface of crystalline powders by heating, and the TCNQ molecule is oxidized, losing CN groups.

(4) The crystallization process and the crystal state of the salts have a great influence upon the thermal stabilities.

(5) In the $Cs_2(TCNQ)_3$ complex salt, the application of the voltage gives rise to a polarization current at a temperature near 200 °C, and the TCNQ molecules tend to migrate in the electric field and to be slightly sublimated at that temperature.

(6) When the voltage is applied to metal–TCNQ salts at temperatures above 150 °C, the salts often suffer irreversible variations in their resistivities.

References

1) S. Yoshimura and M. Murakami, *Ann. N. Y. Acad. Sci.*, **313**, 269 (1978).

2) Y. Kishimoto, T. Hayashi, M. Hashimoto, and T. Ohshima, *J. Appl. Polym. Sci.*, **21**, 2721 (1977).

3) L. R. Melby, R. J. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

4) A. I. Sherle, S. M. Mezhikovskii, V. V. Kuzina, and A. A. Berlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 554 (1974).

5) N. Sakai, I. Shirotani, and S. Minomura, *Bull. Chem. Soc. Jpn.*, **45**, 3321 (1972).

6) W. L. Hawkins, "Polymer Stabilization," Wiley, New York (1972), p. 422.

7) J. S. Blakemore, U. Bernstein, J. E. Lane, and D. A. Woodburg, Int. Conf. Phys. Semecon. (NLD), 13 th, 345 (1976).