

Electrical Conduction in Polyethylene with Semiconductive Electrodes

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ABSTRACT

The electrical conduction characteristics of polyethylene with semiconductive electrodes have been investigated at electric fields of 10 to 600 kV/cm and at temperatures of 25 to 100°C. It was found that the conduction characteristics of the polyethylene were influenced not only by the constituents of the polyethylene but also the electrode materials. Space-charge-limited conduction was found to be the major conduction mechanism in all cases. Differences between conduction characteristics depending on the constituents of the XLPE are described and their causes are discussed.

1. INTRODUCTION

An electrode is essential to assure the application of electrical stress in the measurement of electrical properties. Various electrodes such as vacuum evaporated metals and conductive pastes are used. However, these electrodes are not seen in medium voltage power cables where a semiconductive layer called 'strand shield' exists between the metal conductor and the insulation layer. Therefore, the use of a semiconductive electrode made of the semiconductive compound used for the strand shield may be necessary to simulate the cable situation best.

Different electrical behavior depending on the type of electrode is frequently observed. For instance, Chapeau *et al.* [1] have found that homocharges are developed in polyethylene with a vacuum evaporated metal electrode whereas heterocharges are accumulated with a conductive silicone grease electrode. Ditchi *et al.* [2] have also reported that the composition of the semiconductive compound used as an electrode may be critical in determining the internal charge distribution in XLPE. It seems that the electrical conduction characteristics of the PE are influenced by the electrode materials [3, 4]. More-

over, the breakdown strength of XLPE may be improved by mixing certain additives to the semiconductive compound used for the strand shield [5]. Residual byproducts are also known to change electrical properties such as the charge accumulation characteristics [6, 7]. These data indicate that the dielectric behavior of XLPE with a semiconductive electrode may change with the composition of both the XLPE and the semiconductive electrode.

XLPE may be considered to be composed of three parts: a crosslinked part, a noncrosslinked part and low molecular weight molecules. The crosslinked part is not solvent extractable, having a three-dimensional network structure formed by the curing reaction. The non-crosslinked part essentially is LDPE. The low molecular weight part includes residual byproducts such as acetophenone, cumyl alcohol, and α -methylstyrene [8], and additives such as antioxidants. In addition, XLPE is semicrystalline and may have a variety of morphologies.

Since XLPE is such a complicated material, the interpretation or explanation of the measured electrical properties may be very difficult. This indicates that to get a

better insight into the electrical behavior of XLPE, the contribution of each component may have to be isolated. In this study, therefore, the effects of some of these components on the conduction characteristics of the XLPE have been investigated. In particular, we have explored the effect of electrode materials on the conduction characteristics of LDPE.

2. THEORETICAL BACKGROUND

A power law dependence of the current density J on the electric field E has often been found in many investigations of electrical conduction in insulating polymers. With

$$J = aE^n \quad (1)$$

one finds

$$\ln J = \ln a + n \ln E \quad (2)$$

so that a $\ln J$ vs. $\ln E$ plot is linear with slope n . Various conduction mechanisms are characterized by different values of n . However, a knowledge of n is rarely sufficient to unambiguously identify a conduction mechanism. The case of $n = 1$ (ohmic conduction) is usually the result of field independent values of the carrier concentration and the mobility. The carriers may be either ions or holes or electrons, but must be intrinsic to the material. To be sure that the conduction is truly ohmic, measurements on a single sample are not sufficient. Taking care to keep the electrode area constant, measurements made on a number of samples of different thickness l should yield a current density proportional to V/l where V is the voltage applied across the sample.

Space-charge-limited conduction (SCLC) occurs when the conduction is the result of the injection of excess carriers from an ohmic contact into a material of very low mobility [9]. The concentration of carriers builds up near the injecting contact and reduces the current. In the case of a trap free material one expects

$$J = \frac{9}{8} \frac{\epsilon \mu V^2}{l^3} \quad (3)$$

where ϵ is the relative permittivity and μ is the carrier mobility. In the presence of traps, Equation (3) should be modified as some of the carriers become trapped and do not contribute to conduction. Usually this is taken into account by multiplying the right hand side of the equation by the proportion of carriers in the conduction band. Then when all the traps are filled the SCLC condition as given in Equation (3) is achieved. Again it is important to measure both the field dependence and the sample thickness dependence of the current density.

O'Dwyer [10] has shown that combining the effects of a non-ohmic contact, e.g. a Schottky barrier, with the

effects of space charge results in a current density given by Equation (1) over a limited range of values of the applied field, typically an order of magnitude. In this case values of n range from 2 to 4. Again the sample thickness is important; the value of n is expected to vary with sample thickness. Perlman and Kumar [11] have studied electrical conduction in various polyethylene samples. They have observed SCLC, field dependent mobilities, Poole-Frenkel effects and contact limited injection. Their measurements were made with vacuum evaporated gold contacts on both sides of their samples. The present work is primarily concerned with the effects of various electrodes on the overall conduction in an electrode-polyethylene-electrode sandwich. It is also concerned with the electrical effects of changing the composition of both the polyethylene and the contacts. The considerations outlined here have guided our attempts to identify conduction mechanisms.

3. EXPERIMENTAL

The XLPE used in the present study was prepared by mixing LDPE with 2.0 parts per hundred resin (phr) of dicumyl peroxide. The semiconductive compound used as electrodes is the polyolefin with carbon black and dicumyl peroxide. A small amount of antioxidant, 0.4 phr of Santanox R, was mixed in both materials. Both materials were crosslinked under pressure at 180°C for 20 min. The thickness of the XLPE and of the semiconductive electrode was controlled to be $\sim 40 \mu\text{m}$. The films prepared in this way were either degassed under vacuum to remove the residual byproducts or extracted in such solvents as boiling xylene and chloroform. Boiling xylene was used to remove the extractable part, and chloroform to remove the additives.

The degree of crosslinking after the boiling xylene extraction of XLPE was determined to be 86%. The weight loss of $\sim 14\%$ of XLPE may cause some change in the density and there may be some cavities in the extracted specimen, which may affect the charge formation of the extracted XLPE. In order to reduce such a possibility, the extracted XLPE was again pressed at 180°C for 10 min. and then subjected to testing. The consequences of this procedure were not experimentally evaluated.

The apparatus used to measure the conduction currents is composed of a power supply (± 3 kV(dc) Keithley 247), electrometer (Keithley 617), and test cell. The test cell contains a measuring electrode, the counter electrode and a guard ring. The temperature of 25 to 100°C was controlled in an air convection oven.

Careful attention has to be paid in determining the steady state current as a function of charging time, because the transient current changes for a long period of

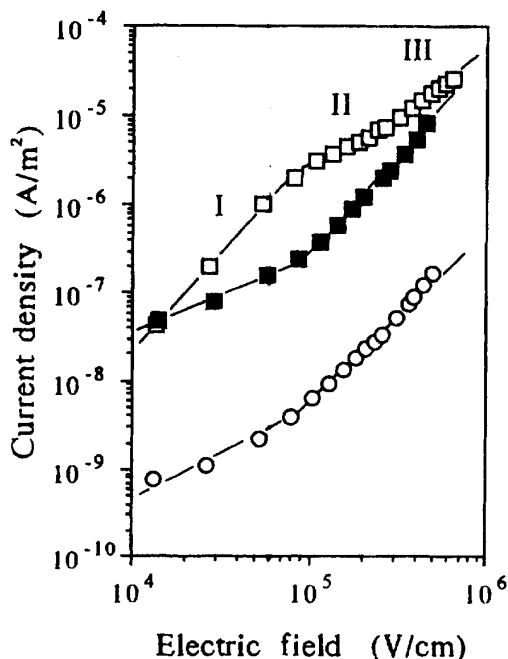


Figure 1.

J - E characteristics of LDPE at 70°C with various contacts: Sputtered Al contact (○), Semiconductive contact (■), Silicone oil contact (□).

time after the application of dc stress [12, 13]. Only a minor change in its magnitude has been reported following a current measurement at 40 min. In this study, therefore, all steady state currents were taken 40 min after the application of dc stress.

4. EXPERIMENTAL RESULTS

4.1. EFFECT OF CONTACTS

Current density - electric field (J - E) characteristics of low density polyethylene (LDPE) at 70°C with various contacts are compared in Figure 1. The contacts used were a silicone oil layer, a semiconductive film, and sputtered Al. The results at other temperatures such as 20, 50 and 90°C showed a trend similar to those at 70°C.

Sputtered Al shows the lowest current density, silicone oil the highest and the semiconductive film lies in between. The shapes of the J - E curves for both sputtered Al and semiconductive contacts are similar. The slopes are ~ 1.0 at low fields below ~ 100 kV/cm and ~ 2.0 at high fields above ~ 100 kV/cm, which suggests that the conduction is governed by an ohmic conduction mechanism at low fields and a SCLC mechanism at high fields. With the silicone oil contact, the slopes in a $\log J$ vs. $\log E$ plot were estimated to be 2.13 at voltages below ~ 100 kV/cm (Region I), 1.86 at voltages

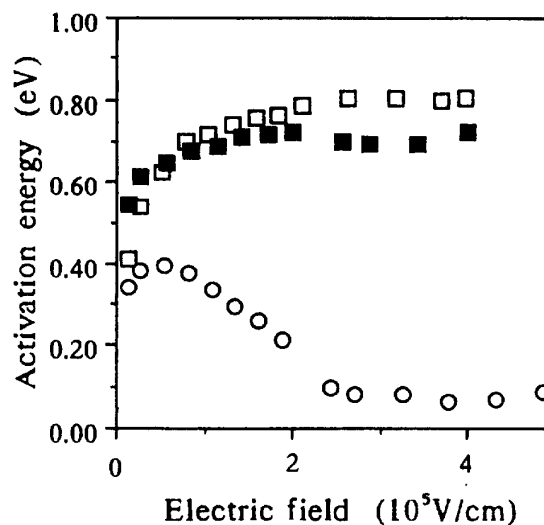


Figure 2.

Activation energy for various contacts: Sputtered Al contact (□), Semiconductive contact (■), Silicone oil contact (○).

above ~ 300 kV/cm (Region II), and 1.30 at voltages of 100 to 300 kV/cm (Region II). The rate of change of current density is considerably suppressed at voltages of ~ 300 kV/cm with this contact.

Differences in activation energy depending on the type of contact are demonstrated in Figure 2. Sputtered Al shows the highest, semiconductive contact an intermediate, and silicone oil contact the lowest activation energy. The activation energy using sputtered Al was estimated to be ~ 0.8 eV, which agrees well with the published value [4]. A slight or no decrease in activation energy as a function of voltage is observed in both sputtered Al and semiconductive film contacts while a large decrease is observed when the silicone oil contact is used.

The silicone oil used in this study is an insulating oil. Surprisingly, the results with the silicone oil were found to be very different from those with other contacts. It is strongly believed that the silicone oil penetrated the polymer, which seems to be quite possible because the silicone oil consists of low molecular weight molecules. Then the conduction characteristics may change. In order to prove this possibility, both surfaces of the specimen after testing were washed to remove the remaining silicone oil and then subjected to a FTIR-ATR analysis. However, no appreciable differences between the control specimen and the tested specimen were observed, which suggests that no appreciable amount of silicone oil has penetrated the polyethylene. The exact reasons for such different behavior with the silicone oil remain open for discussion.

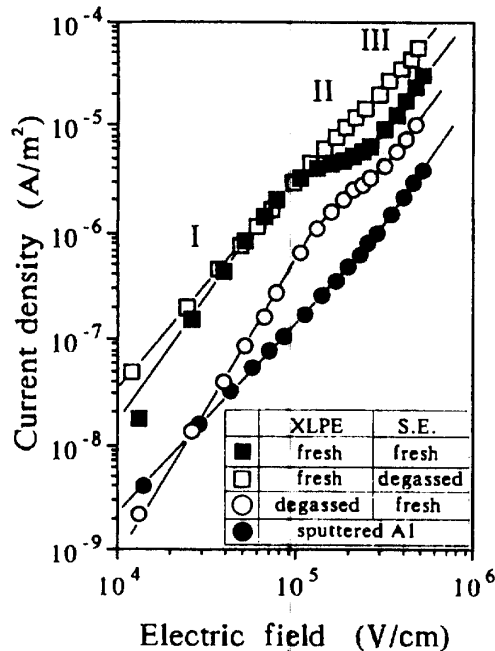


Figure 3.

J-E characteristics of XLPE with semiconductive electrodes at 90°C.

4.2. EFFECTS OF TREATMENT OF XLPE AND SEMICONDUCTIVE ELECTRODE

The effect on the conduction behavior of the presence of the byproducts of the crosslinking reaction in both XLPE and the semiconductive electrode was investigated. The specimens considered in this study are: fresh XLPE with fresh semiconductive electrode (XFSF), fresh XLPE with vacuum treated semiconductive electrode (XFSV), vacuum treated XLPE with fresh semiconductive electrode (XVSF), and fresh XLPE with sputtered Al electrode (XFAI).

Figure 3 compares the *J-E* characteristics of the XLPE with semiconductive electrode at 90°C. All *J-E* curves except the case of XFAI can be divided into three regions: I, II, and III, the slopes of which are summarized in Table 1. As shown in Figure 3 and Table 1, all XLPE with a semiconductive electrode show a decrease in the rate of change of current density with field in Region II, the extent of which depends on the sample treatment. A considerable suppression in Region II was found with the XFSF, a slight suppression with the XFSV, and an intermediate suppression with the XVSF. None was observed with the XFAI.

A classical method to identify the conduction mechanisms is to determine the slope of a $\log J$ vs. $\log E$ plot, as discussed in Section 2. A slope of 2 of the $\log J$ vs.

Table 1.

Slopes in a $\log J$ vs. $\log E$ plot for XLPE. (NA: not available)

Region	XFSF	XFSV	XVSF	AFAI
I	1.8	1.7	2.0	1.8
II	0.4	0.9	1.4	NA
III	2.3	2.2	2.3	2.2

$\log E$ plot suggests SCLC, which may be the case for Region I of all XLPE with the semiconductive electrodes regardless of their condition (See Table 1). However, the assignment of conduction mechanisms for Regions II and III can not be made readily.

In order to confirm the SCLC mechanism, the thickness dependence of current density was studied, the results of which are shown in Figure 4. We see that all XLPE show linearity in a \log (current density) vs. \log (specimen thickness) plot for all regions. These results indicate that SCLC is the major conduction mechanism for XFSF, XFSV, and XVSF over electric fields ranging from 10 to 600 kV/cm.

One can notice from Figure 4 that the slopes are -3 for the XFSF and -2 for both XVSF and XFSV. Trap-free SCLC with negligible thermally generated charge carriers can be characterized by a -3 power dependence between the current density and the sample thickness. On the other hand, when traps are involved, the -3 power dependence is usually not obtained. Therefore, it can be concluded that SCLC is the major conduction mechanism for XLPE with semiconductive electrodes and that traps may be introduced by vacuum treatment. However, details of the nature of the traps introduced are not known at this moment.

4.3. LDPE vs. XLPE

J-E curves of fresh LDPE with fresh semiconductive electrode at 70°C and fresh XLPE with fresh semiconductive electrode at 90°C are compared in Figure 5. Two features are prominent. One is that the decrease in rate of change of current density with field is found only in the XFSF. The other is that the LDPE shows ohmic conduction at low fields and the SCLC mechanism at high fields while the XFSF shows only SCLC, as described in the previous Sections. In addition, the XFSF shows a higher value of current density compared to the LDPE.

4.4. EFFECT OF SOLVENT EXTRACTION OF XLPE

The conduction behavior of the XLPE was further evaluated with solvent-extracted XLPE in order to understand the effects of the presence of various components. The boiling xylene extracted XLPE was used to

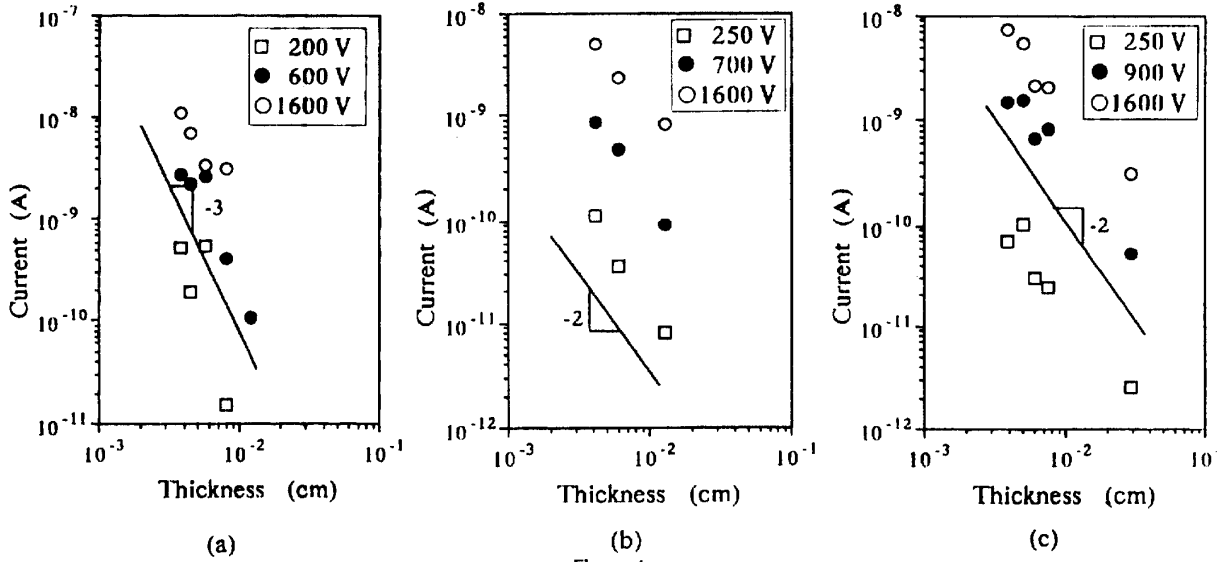


Figure 4.

A thickness dependence of the steady current of XLPE with semiconductive electrodes. (a) XFSF, (b) XFSV, (c) XVSF.

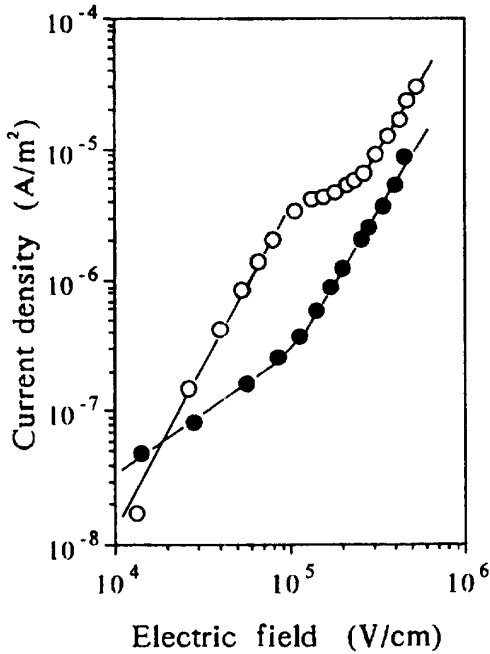


Figure 5.

J-E characteristics of LDPE at 70°C (●), XLPE at 90°C (○) with fresh semiconductive electrodes.

evaluate the conduction behavior of the pure crosslinked component and the chloroform-extracted XLPE was used to get rid of the effect of the additives.

The *J-E* characteristics of boiling xylene extracted

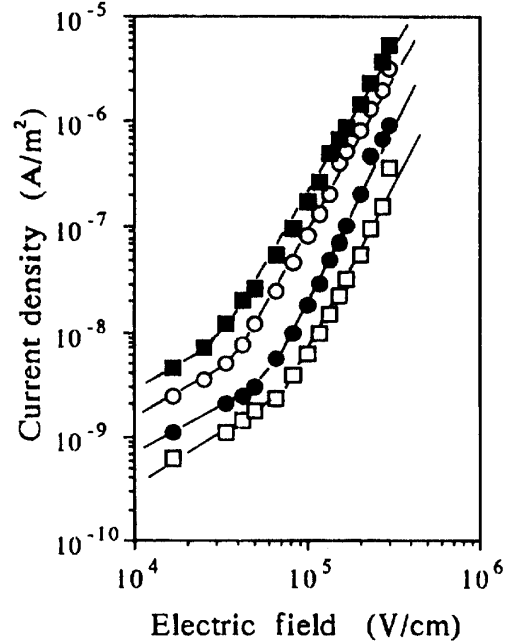


Figure 6.

J-E characteristics of boiling xylene extracted XLPE with vacuum degassed semiconductive electrodes: 50°C (□), 70°C (●), 90°C (○), 100°C (■).

XLPE are shown in Figure 6. A monotonic increase of the current density as a function of applied electric field was found. That is, the decrease in dJ/dE at high fields

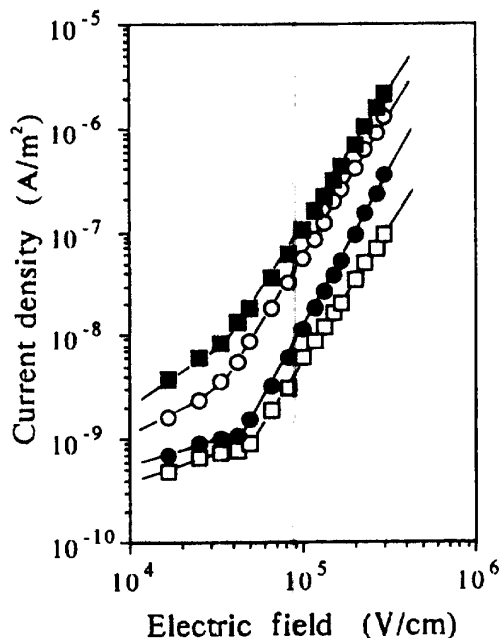


Figure 7.

J-E characteristics of chloroform-extracted XLPE with vacuum degassed semiconductive electrodes: 50°C (□), 70°C (●), 90°C (○), 100°C (■).

which was a typical feature of XFSF was not found in this specimen. Similar features, i.e. a linear relation between $\log J$ and $\log E$ and no change in dJ/dE , were observed with the chloroform-extracted XLPE, as shown in Figure 7.

A separate evaluation of the thickness dependence of current density shows $J \propto l^n$ where $n = -2$ to -3 for both solvent-extracted XLPE. This result, combined with the observation of the linearity between $\log J$ and $\log E$, indicates that SCLC may be the major conduction mechanism in solvent-extracted XLPE. As shown in Table 2, the slopes in a $\log J$ vs. $\log E$ plot are 3.0 to 3.5 for boiling xylene extracted XLPE and 2.6 to 3.0 for chloroform-extracted XLPE. These values suggest that the trap depth may be distributed, as pointed out by O'Dwyer [10] and Lampert and Mark [14].

5. DISCUSSION

THIS study was initiated to investigate mainly the effects of such components as byproducts, additives, and the non-crosslinked portion on conduction characteristics of XLPE. The effects of electrode materials on the conduction characteristics of LDPE were also studied.

The major features observed in the present study are (1) conduction characteristics of polyethylene are influ-

Table 2.
Slopes in a $\log J$ vs. $\log E$ plot for solvent-extracted XLPE

Solvent	50°C	70°C	90°C	100°C
Xylene	3.2	3.5	3.1	3.0
Chloroform	2.6	3.0	2.7	2.6

enced not only by the electrode materials but also by the condition of the XLPE and the semiconductive electrode, (2) SCLC is the major conduction mechanism at high fields for both LDPE and XLPE, and (3) a change in dJ/dE at certain field range was found in such systems as LDPE with a silicone oil contact and XLPE with a semiconductive electrode. Of these, the first two features are the ones that are readily explainable based upon published information. The third feature, a change in dJ/dE , is of particular interest in this study, and we discuss its origin further.

A change in a dJ/dE has been reported with polyethylene and other polymers [15-20]. For example, polyethylene in single crystal form and in the molten state is known to show such a change [15, 16]. Polypropylene and PVDF are also known to possess similar features [17-20]. Speculatively, this behavior has been attributed to (1) morphological changes caused by high electric field, (2) heterocharge formation, (3) bipolar injection and (4) change of hopping distances. It has been observed in the present study that the extent of the change in dJ/dE depends on the particular treatment of the specimen. Vacuum degassing reduces the extent of change and solvent-extracted XLPE shows no such change. Besides, LDPE with a silicone oil contact does show such change. Vacuum degassing surely removes the byproducts of the crosslinking reaction efficiently and it is expected that silicone oil may diffuse into the LDPE at high temperatures. Considering all these facts, we conclude that the change in dJ/dE is most likely caused by the low molecular weight species including the residual byproducts and additives.

Boiling xylene extracted XLPE is composed of the crosslinked part only while chloroform-extracted XLPE contains the crosslinked part and the non-crosslinked part but without the low molecular weight mobile species such as additives and byproducts. Thus, the difference between these two solvent-extracted XLPE is the LDPE component. This fact, combined with the observation of a linearity in a $\log J$ vs. $\log E$ plot, indicates that the LDPE component does not cause the saturation of current density at certain field range. At this moment, however, the present results cannot provide a clear explanation as to why these low molecular weight species cause such change in dJ/dE , and further work is needed.

It is known that the $\log J$ vs. $\log E$ for trap-free SCLC

is characterized by a slope of 2 whereas the distributed trap SCLC is represented by slopes of 2 to 6 [10, 14]. As shown in Table 2, the chloroform-extracted XLPE shows slopes of 2.5 to 3.0 whereas boiling xylene extracted XLPE shows slopes of 3.0 to 3.5. In addition, the XFSV shows the slopes of 1.7 and 2.2 at 90°C. These results suggest that the traps are associated with low molecular weight molecules of XLPE. It seems, therefore, that the nature of traps of the pure crosslinked part of the XLPE is modified by the LDPE component in the XLPE and further modified by the additives and byproducts. The modification seems to be made in the direction of forming trap-free SCLC from the distributed trap SCLC. The trap-free SCLC is achieved in the presence of additives and byproducts.

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