

## 반도전 전극을 사용한 가교폴리에틸렌의 전기전도현상

서 광 석·이 창 용·이 미 경\*

고려대학교 공과대학 재료공학과 · \*한국과학기술원 고분자공정연구소  
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## Electrical Conduction of XLPE with Semiconductive Electrodes

Kwang S. Suh, Chang R. Lee, and Mikyung Lee\*

Department of Materials Science, Korea University, Seoul 136-701, Korea

\*Polymer Processing Lab., KIST, Seoul 130-605, Korea

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**요 약 :** 반도전성 전극을 사용하여 10~600 kV/cm의 전기장 및 25~100°C의 온도영역에서 가교폴리에틸렌의 전기전도특성에 대하여 연구하였다. 연구결과, 반도전성 전극을 사용한 모든 가교폴리에틸렌은 일정 영역의 전기장에서 전류밀도의 증가율이 감소하는 현상을 가지며 감소정도는 반도전성 전극의 상태에 크게 좌우된다는 사실을 알았다. 진공처리하지 않은 반도전성 전극의 경우 전류밀도 증가율의 감소가 가장 현저하였으며 반도전성 전극을 진공처리한 경우에는 약간의 감소현상만이 관찰되었다. 또한 가교폴리에틸렌의 전도기구도 반도전성 전극의 상태에 따라 다르게 나타나는 것으로 관찰되었다. 높은 전기장에서의 전기전도기구의 경우 진공처리하지 않은 경우 일반적으로 공간전하제한전도(SCLC) 기구만이 주된 전도기구인 반면에 반도전성 전극을 일단 진공처리하면 SCLC에서 Schottky 전도기구로 바뀌는 현상이 관찰되었다. 이 두 현상 모두 반도전성 전극 내에 함유되어 있는 가교반응시 과산화물의 열분해에 의하여 발생한 저분자량의 부산물과 밀접한 연관이 있는 것으로 생각된다.

**Abstract :** Electrical conduction characteristics of the XLPE with semiconductive electrodes have been investigated at electric fields ranging from 10 to 600 kV/cm over the temperature range of 25 to 100 °C. It was found that the rate of change of current density was suppressed at a certain field range, the extent of which depends strongly on the conditions of semiconductive electrodes. As-pressed semiconductive electrode produced the most considerable suppression and vacuum treated ones only slight suppression. At high fields above a few hundreds kV/cm, the conduction mechanisms change from the space-charge limited conduction(SCLC) to the Schottky conduction once the semiconductive electrodes are treated under vacuum. A suppression in a rate of change of current density and the change of conduction mechanisms were attributed to the low molecular weight byproducts formed by the thermal decomposition of peroxide during the crosslinking reaction.

## INTRODUCTION

In measuring voltage-related properties, various types of electrodes such as vacuum evaporated metals and silver pastes are used for applying voltages to the specimen. Two major criteria in selecting the proper electrode are (1) whether it can provide the ohmic or blocking contact and (2) how the contact potential can be reduced.

In some cases, however, these factors may have to be ignored in actual experimentations. A typical example can be found in medium and high voltage power cables, where a so-called conductor strand shield exists between the metal conductor and the insulation layer. This strand shield is the crosslinked polyolefin with a high content of carbon black and acts as a layer to diminish a sudden voltage drop between the metal conductor and the insulation layer and to prevent a direct contact of the insulation layer with the metal strands. In this case, for example, one may encounter the situation where the results obtained with such electrodes as vacuum evaporated metals and silver pastes may not be utilized directly for predicting the insulation properties of the materials for cable insulations. A modification in electrical conduction characteristics of polyethylene due to different contacts has been already reported in our previous publications.<sup>1,2</sup> It can be said, therefore, that a semiconductive electrode made from the same material as the one for the strand shield needs to be selected so as to simulate best the situation encountered in power cables.

In this study, therefore, dc conduction characteristics of both fresh and vacuum degassed XLPE and semiconductive electrodes were investigated and compared with those of sputtered Al electrodes.

## EXPERIMENTAL

About 40  $\mu\text{m}$  thick XLPE films were prepared by compression molding from a commercially available XLPE, a major insulating material for medium

voltage power cables. Semiconductive compound produced by Dong Sun Material Co. Ltd. was compression molded to about 40  $\mu\text{m}$  thick films and physically attached to both surfaces of XLPE film. This compound, the olefinic polymer containing a large amount of carbon black and various additives, is the same material as the one which is being used in cable manufacturing industries as a strand shield of power cables. Both materials were treated in a vacuum oven, details of which are summarized in Table 1.

Of these, XLPE1 to XLPE3 have been chosen to study the effects of conditions of both XLPE and semiconductive electrodes and XLPE4 to compare the effect of electrode types.

J-E(current density-electric field) characteristics of these specimens were determined at temperatures from 25 to 100°C by measuring 30 minute charging currents after the application of dc voltages. Details on both instrumentation and experimentation have been described elsewhere.<sup>1</sup>

## ANALYSIS OF CONDUCTION MECHANISMS

An analysis of conduction mechanisms from J-E curves is well documented in the literature.<sup>3-7</sup> When a linearity in a log J vs. log E plot holds true, current densities and electric fields can be expressed as  $J \propto E^n$ , where n is a slope in a double logarithmic plot of J and E and can be utilized in differentiating the conduction mechanisms. That is, n=1 represents the ohmic conduction and n=2 the SCLC. The SCLC mechanism can be confir-

**Table 1.** Conditions of XLPE Specimen and Semiconductive Electrodes

	XLPE1	XLPE2	XLPE3	XLPE4
XLPE	fresh <sup>1</sup>	fresh	vac. treated	fresh
Semicond. electrode	fresh	vac. treated <sup>2</sup>	fresh	sput. Al <sup>3</sup>

<sup>1)</sup> Tested within a few hours after the compression molding

<sup>2)</sup> Under vacuum at 80°C for 100 hours.

<sup>3)</sup> Sputtered Al

med by a thickness dependence of conduction currents. That is, for the SCLC,  $J \propto d^{-3}$  following a Child law. However, if a  $\log J$  vs.  $\log E$  curve deviates from the linearity, a field dependence of conduction mechanisms shown in Table 2 needs to be examined for a correct identification of conduction mechanisms. Typical mechanisms which belong to this category are Schottky, Poole-Frenkel, or Tunneling(Fowler-Nordheim) mechanisms.

### RESULTS

#### XLPE(Fresh)-Semiconductive Electrode(Fresh)

Figure 1 shows J-E characteristics of the fresh XLPE with the fresh semiconductive electrode (hereafter XLPE1). The current density increases, for example roughly from  $10^{-9}$  to  $10^{-5}$  A/m<sup>2</sup> at 70°C as the electric field increases from 10 to 600 kV/cm. Also, higher current densities were obtained at higher temperatures.

In Fig. 1, four regions having different rate of change of current density are observed. These are assigned as Region I, II, III, and IV in the order of increasing field. At low temperatures, for example at 25°C, the slope changes from 1 to about 2, which indicates that the conduction mechanisms change from the ohmic to the SCLC. At higher temperatures, the situation becomes a little different. In the case of 100°C result, the slopes are 1.9 for Region II, 0.4 for Region III, and 2.15 for Region IV. It can be said, therefore, that the SCLC mechanism is predominant for Region II and IV and that the conduction mechanism for Region III is apparently different. However, a thickness dependence of current density shown in Fig. 2 indicates that the

SCLC may be the main conduction mechanism for Region II, III, and IV.

#### XLPE(Fresh)-Semiconductive Electrode (Vacuum Treated)

Figure 3 shows J-E characteristics of the fresh XLPE with the vacuum-treated semiconductive electrode (hereafter XLPE2). One can see that at 25°C the slope, n, is equal to 1 below about 50 kV/cm above which n becomes approximately 2.0. This indicates that the conduction mechanism changes from the ohmic to the SCLC at about 50 kV/cm. Also, a 50°C result shows the change from the ohmic to the SCLC at about 30 kV/cm, a little lower than that of a 25°C result. Above 50°C, however, only SCLC mechanism can be seen over the low electric fields.

At higher fields, on the other hand, the rate of change of current densities deviates slightly from the linearity, which implies that the conduction mechanism other than the SCLC may work in this region and that the field dependence needs to be examined. For this purpose, the current densities at higher fields have been rearranged in a  $\log J$  vs.  $E^{1/2}$  plot, a so-called Schottky plot. As shown in

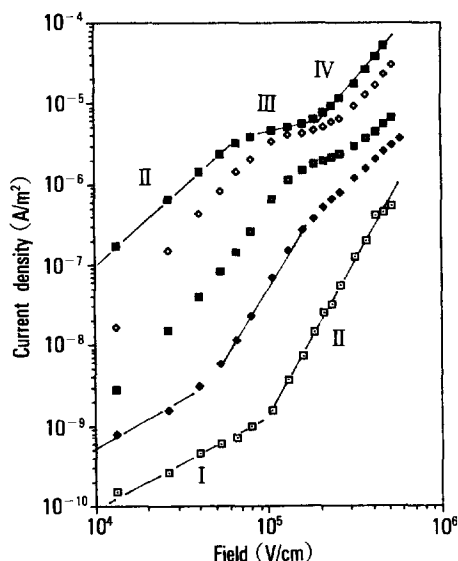


Fig. 1. J-E characteristics of the fresh XLPE with the fresh semiconductive electrode : Temperatures : 25°C (□), 50°C(◆), 70°C(■), 90°C(◇), 100°C(■).

Table 2. Field Dependence of Conduction Mechanisms

Conduction Mechanisms	Field Dependence
Schottky	$J = AT^2 \exp\{(\beta_s E^{1/2} - \phi)/kT\}$
Tunneling	$J = AE^2 \exp(-B/E)$
Poole-Frenkel	$\sigma = \sigma_0 \exp\{(\beta_{PF} E^{1/2} - \phi)/kT\}$
SCLC	$J = (9/8) \epsilon \epsilon_0 \mu_{eff} V^2/d^3$
Hopping	$J = J_0 \sinh(eEa/2kT)$

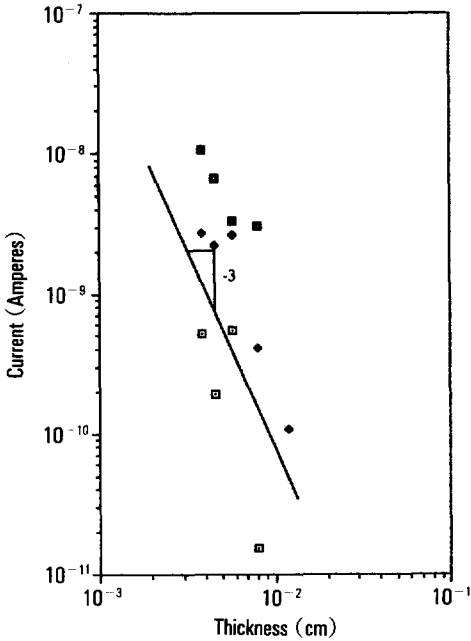


Fig. 2. A thickness dependence of charging current of the XLPE with the semiconductive electrode : 200 V ( $\square$ ), 600 V ( $\blacklozenge$ ), and 1600 V ( $\blacksquare$ ).

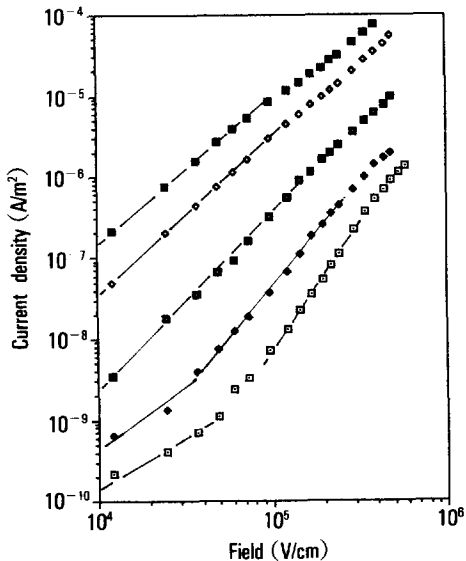


Fig. 3. J-E characteristics of the fresh XLPE with the semiconductive electrode treated under vacuum at 80 °C for 100 hours : Temperatures : same as in Fig. 1.

Fig. 4, a linearity in a Schottky plot was obtained, which suggests that the conduction is limited by a so-called Schottky effect in this region. Schottky coefficient,  $\beta_s$ , was estimated from the slope of Fig. 4 to be  $1.53 \times 10^{-24}$ , which is in the same order as the calculated value from  $\epsilon=2.3$  for the XLPE.

**XLPE(Vacuum Treated)-Semiconductive Electrode(Fresh)**

Figure 5 shows the J-E curves for the XLPE treated under vacuum at 80°C for 100 hours with the fresh semiconductive electrode (hereafter XLPE3). General features including the conduction mechanisms are almost the same as those observed with the XLPE1. For example, four regions are distinguishable and a suppression in a rate of current density was observed. The ohmic conduction mechanism seems to be the major one at low fields and the SCLC at higher fields.

In this case, however, the extent of suppression in a rate of change of current density is not significant compared to that of the XLPE1. This can be seen from the slope of Region III, i.e., 0.416 for the XLPE1 and 0.959 for the XLPE3.

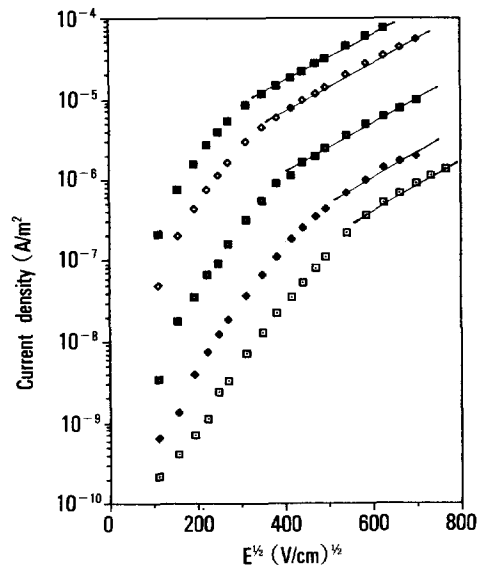


Fig. 4. The Schottky plot of the fresh XLPE with the semiconductive electrode treated under vacuum at 80 °C for 100 hours : Temperatures : same as in Fig. 1.

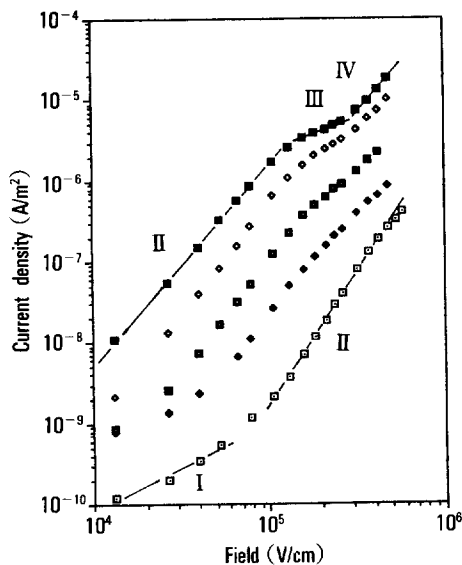


Fig. 5. J-E characteristics of the XLPE treated under vacuum at 80°C for 100 hours with the fresh semiconductive electrode : Temperatures : same as in Fig. 1.

#### XLPE(Fresh)-Sputtered Al Electrode

J-E characteristics of the XLPE with the sputtered Al electrode (hereafter XLPE4) are shown in Fig. 6. It can be seen that at 25°C the slope changes from 1 to about 2, which indicates that the conduction mechanisms change from the ohmic to the SCLC. At higher temperatures no ohmic conduction region is seen.

At higher fields for all temperatures the rate of change of current densities deviates from the linearity, so that a Schottky plot was made in Fig. 7 to identify the conduction mechanism. A Schottky plot shown in Fig. 7 exhibits a linear relation between  $\log J$  and  $E^{1/2}$ , so that it can be suggested that the conduction at high fields is limited by the Schottky mechanism.

#### DISCUSSION

Some of the features observed in the present study agree well with those that have been already published.<sup>8-10</sup> Also, these features are the ones observed in all specimens with the semiconductive

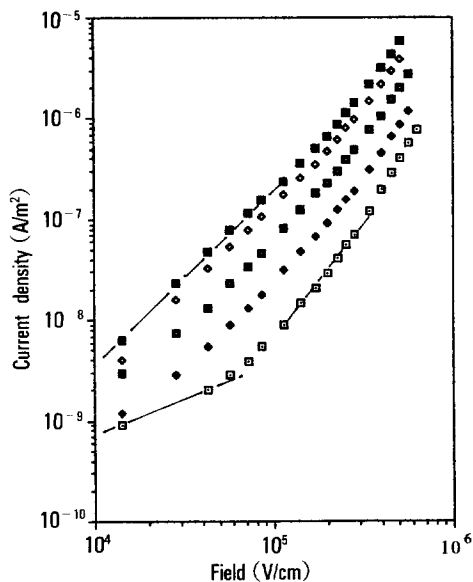


Fig. 6. J-E characteristics of the fresh XLPE with the sputtered Al electrode : Temperatures : same as in Fig. 1.

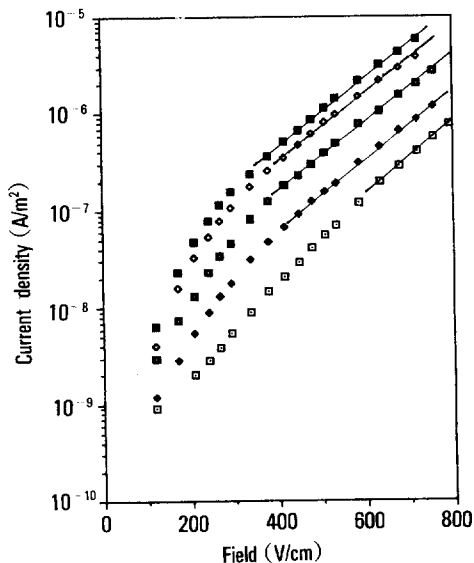


Fig. 7. The Schottky plot of the fresh XLPE with the sputtered Al electrode : Temperatures : same as in Fig. 1.

electrodes. For example, the current density increases as both electric field and temperature increase. Also, upto medium fields, the ohmic and the

SCLC are the major conduction mechanisms. At low temperatures below 50°C the conduction mechanisms change from the ohmic to the SCLC, whereas at high temperatures above 70°C the SCLC is the major conduction mechanism.

On the other hand, there observed two features showing a systematic change depending on the conditions of semiconductive electrodes. These are (1) a suppression in a rate of change of current density and (2) change of conduction mechanisms, characteristics of which are compared in Table 3.

#### Suppression in a Rate of Change of Current Density

As shown in Table 3, a suppression in a rate of change of current density at a certain field range is observed in all specimens with the semiconductive electrodes, the extent of which seems to depend on whether the semiconductive electrode is fresh or treated under vacuum. A considerable suppression was observed with the fresh semiconductive electrode, whereas a slight suppression with the vacuum treated one. No such suppression is observed with the sputtered Al electrode. A similar phenomenon has been observed in silicone-oil pasted LDPE<sup>1,2</sup> as well as in other polymers.<sup>11~16</sup>

Regarding the source for such suppression, the information in Table 3 is informative. That is, such suppression may come from the low molecular weight species residing in semiconductive electrodes. In a fresh semiconductive electrode, there exists such byproducts of peroxide decomposition as acetophenone, cumene, moisture, methane,  $\alpha$ -methylstyrene.<sup>6</sup> It has been also reported that the concentrations of these byproducts are reduced greatly by the vacuum treatment.<sup>17</sup> Under these circumstances, the migration of byproducts into the XLPE may be considerable in case of the fresh semiconductive electrode and not significant in case of the vacuum treated one.

These low molecular weight byproducts may be charged under desirable conditions and form the heterocharges. High electric fields may enhance the migration of these charges toward the counter electrode side. The accumulation of heterocharges

**Table 3.** Conduction Characteristics of XLPE with Semiconductive Electrodes

	XLPE1	XLPE3	XLPE2	XLPE4
XLPE	fresh	vac. treated	fresh	fresh
Semicon. Electrode	fresh	fresh	vac. treated	sput. Al
Slope in Region III	0.416	0.959	1.404	NA
Conduction Mechanism	Only SCLC		Change from SCLC to Schottky	
Schottky Coeff.	NA		$1.5 \times 10^{-24}$	$1.8 \times 10^{-24}$

in polyethylene has been already reported.<sup>17,18</sup> Thus formed heterocharges may neutralize the homocharges coming from the electrode, the net result being a suppression in a rate of change of current density.

#### Change of Conduction Mechanisms at High Fields

Conduction mechanisms also depend on whether the semiconductive electrodes are as-pressed or treated under vacuum. With fresh semiconductive electrodes, even when the rate of change of current density was considerably suppressed in a certain field range, the SCLC mechanism remains unchanged over the entire range of electric field. With vacuum treated semiconductive electrodes, on the other hand, the conduction mechanisms change from the SCLC to the Schottky mechanism.

Since the change of conduction mechanisms is observed only with the vacuum treated semiconductive electrodes, it can be easily deduced that the byproducts play a very important role in determining conduction mechanisms. When the semiconductive electrode without low molecular weight byproducts are used as a contact, the conduction is governed mainly by the homocharges injected from the electrode as is the case in sputtered Al electrode. However, the byproducts chargeable and mobile under strong electric field seem to reduce the amount of homocharges, possibly by the neutralization effect, so that the conduction is still governed by the space charges residing in the XLPE.

In conclusion, the presence of byproducts in semiconductive electrodes surely influences the conduction characteristics of the XLPE. The present results also suggest that the electrode materials need to be carefully selected for a correct characterization of electrical behaviors of the system. A wrong choice of electrode material may lead to an observation of different conduction characteristics and consequently to a misunderstanding. A similar concept may be extended to both measurement and interpretation of other charge-related electrical properties.

### CONCLUSIONS

Conduction characteristics of the XLPE were found to change depending on the conditions of semiconductive electrodes. The major conclusions are as follows :

1. It was generally observed that the current density increases as both field and temperature increase.

2. At low fields below a few tens kV/cm, the ohmic conduction arising from the internally existing ionic species was a major conduction mechanism. On the other hand, the SCLC mechanism seems to play a major role at medium fields up to a few hundreds kV/cm.

3. Conduction mechanisms at high fields also depend on conditions of semiconductive electrodes. With the fresh semiconductive electrodes, the SCLC is the major conduction mechanism, whereas the mechanisms change from the SCLC to the Schottky with the vacuum treated ones.

4. A suppression in a rate of change of current density was observed regardless of conditions of semiconductive electrodes. However, the extent of such suppression depends on the concentration of byproducts formed during the crosslinking reaction. A considerable suppression was found with the fresh semiconductive electrodes and a slight suppression with the vacuum treated ones.

5. The change of conduction mechanism and a

suppression in a rate of change of current density were attributed to the low molecular weight byproducts formed by the thermal decomposition of peroxide during the crosslinking reaction.

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