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Nonlinear DC response in high-density polyethylene/graphite nanosheets composites

WEI LU, DAJUN WU, CUILING WU, GUOHUA CHEN*
Department of Materials Science and Engineering, Huaqiao University, Quanzhou 362021, China
E-mail: hdcgh@hqu.edu.cn

In this paper, the nonlinear conduction behavior of high-density polyethylene (HDPE)/graphite nanosheets composites above the percolation threshold was investigated. For some samples, the I–V curves are smooth and the nonlinear term is cubic, rather than quadratic. However, for other samples, the onset of nonlinearity is accompanied by the appearance of steps in I–V curves. Furthermore, the crossover current I_c for two types of curves at which nonlinearity occurs scales with the linear conductance Σ_1 as $I_c \sim \Sigma_1^x$, with $x \approx 1.28$. And the second-order conductance, Σ_2, also scales with Σ_1 as $\Sigma_2 \sim \Sigma_1^y$, with $y \approx 1.00$. Two classical models, NLRRN (nonlinear random resistor network) and DRRN (dynamic random resistor network), cannot fully explain our experimental results. It is likely that a combination of these two models may account for the nonlinear feature better. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Recently, composites based on conducting fillers dispersed within insulator matrices have been the subject of both theoretical and experimental studies. Characteristics features in such disordered media are nonlinear conduction behavior and its enhancement in the vicinity of the percolation threshold where a spanning conductive network appears for the first time and many physical quantities (i.e., electrical conductance) become unsteady [1]. Moreover, composites with highly nonlinear current voltage relationship were used to develop varistors for protecting against transient overvoltages [2]. Consequently, there exists a strong motivation for studying these intriguing features for further understanding and possible practical applications [2].

Generally speaking, two kinds of nonlinear transports in such conducting mixtures of an insulator and a conductor can be distinguished. One is electrical failure taking place irreversibly in extreme conditions either due to application of high voltage (dielectric breakdown [3]) or current (burning of fuse [4]), namely, irreversible nonlinearities. The other kind corresponds to the phenomenon that electrical conduction becomes reversibly nonohmic (nonlinear) because of application of small bias of voltage or current [5], that is, reversible conduction. Such reversible nonlinear transports are in the subject of this study.

Nonlinearity in disordered composites may arise in two ways. In one case, the conducting elements may be intrinsically nonlinear [6], and in another, the conducting elements are ohmic but macroscopic conductance becomes nonlinear due to possible appearance of additional channels resulting from tunneling or hopping in disordered media within insulating regions [5]. However, the nonlinearity, in both cases, is enhanced as P (volume fraction of conducting phase) tends towards P_c (the percolation threshold of the composites) either from below (as in normal–super conductor mixtures [7]) or from above (as in conductor-insulator mixtures [8]).

Following detailed diagram was proposed to illustrate nonlinear conduction in disordered media at a fixed T (temperature) and P (volume fraction of conducting phase) close to the percolation threshold [9]. It can be seen that, from the below figure, Σ is practically constant in the linear regime (a); a crossover from linear to nonlinear regime at a bias V_0 (onset voltage) occurs, as V is increased; the conductance still increases at a lower rate and approaches a constant value corresponding to saturated state (b); the c region is actually the Joule or irreversible region in which application of high current causes Σ to decrease gradually before irreversible state of breakdown or destruction.

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*Author to whom all correspondence should be addressed.

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TABLE I Symbols and denotations

Symbols and denotations	Meaning
Σ	conductance
Σ_1	linear conductance
Σ_2	second order conductance
I_c	crossover current
V_c	crossover voltage
ρ	resistivity
P	volume fraction
P_c	percolation threshold
t	conductivity exponent
v	correlation length critical exponent
L	sample size
ξ	correlation length
d	dimensionality of the composite
r	constant
A	constant
x	exponent
y	exponent
b	exponent
z	V/V_c
NLRRN	nonlinear random resistor network
DRRN	dynamic random resistor network
NLRDRN	nonlinear random dynamic resistor network
HDPE	high-density polyethylene

However, surprisingly, reversible nonlinear conduction has not received sustained attention of the people working with disordered composites, compared with temperature-dependent nonlinearity [9, 10]. Based on studying the nonlinear behavior of a two dimensional system of the gold films near percolation threshold, Gefen *et al*. [5] found that I_c (crossover current) and Σ_1 (linear conductance) obeyed a scaling relationship. Furthermore, two theoretical models for onset of nonlinear conduction, nonlinear random resistor network (NLRRN) and dynamic random resistor network (DRRN), were offered to explain the deviation from linear characteristics and the power law for the crossover point. And the experimental results of gold films were in fair agreement with predictions of DRRN model, however, Chen *et al*. [11] reported that neither of these two models could account for the nonlinearity of I–V curves of nylon-6/FG composites.

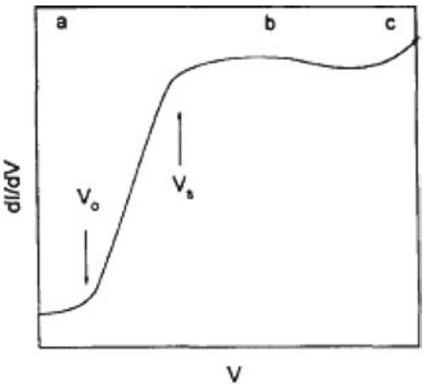

Figure 1 Nonlinear conduction behavior of conductance Σ as a function of the bias V at fixed T and P.

In this paper, we focus on the reversible nonlinear I–V characteristics of HDPE/graphite nanosheets nanocomposites above the percolation threshold and applicability of these two models mentioned above. We will show that it is impossible, through the application of two classical models, to completely interpret the nonlinear conduction behavior in our case.

2. Experimental procedures

2.1. Materials

The conductive filler used here consists of graphite nanosheets with an average thickness of about 50 nm and an average diameter of about 12 μm. High-density polyethylene (HDPE) ($\rho = 0.95$ g/cm^3, melting point = 120°C) is supplied by Petrochemical Ind. Co. Ltd.

2.2. Fabrication of HDPE/graphite nanosheets nanocomposites

Detailed procedures and conditions for elaboration of graphite nanosheets were described in our previous papers [12, 13]. The HDPE/graphite nanosheets composite was prepared via a two-roll mill. Brief procedures were as follows: preweighed HDPE and graphite nanosheets were mixed on a two-roll mill and then molded to form sheet samples with 20 mm in length, 15 mm in width and 1.5 m in height.

2.3. Measurements

Seven samples were measured in this paper. The resistances of seven samples were fitted to the relation [1] $\rho \sim (p - p_c)^{-t}$, where t is conductivity critical exponent and p_c is the percolation threshold. And we found that p_c is 0.11 by volume and t is 3.02.

Measurements of the I–V characteristics 25°C were performed in the axial direction and at. An YJ78 direct-current standard voltage generator (Shanghai No. 2 Electrometer Factory) was used as the voltage source. To ensure good contact conductive paint was applied on the flat surfaces of the samples hold between two circular brass electrodes. To minimize Joule heating, the effective current through the samples was recorded immediately after a voltage was applied. V and I were collected with two DT9205 A (Haidi, Shenzhen, China) meters.

3. Theory

The first model proposed to account for current-voltage nonlinearity in disordered composites is a random resistor network of intrinsically nonlinear resistors, which is referred to as nonlinear random resistor network [5]. Assuming that each resistor has a small, nonlinear component, the current-voltage characteristics can be expressed as following:

$$V = \mathrm{rI} - \mathrm{AI}^{\alpha} \tag{1}$$

where r and A are constants and α is an exponent greater than 1. For sufficiently small application of current, the conduction behavior is considered to be linear. The crossover current, beyond which the overall conductance deviates from the linear conductance, is defined:

$$I_c \sim (r/|A|)^{1/(\alpha-1)} \tag{2}$$

The second model, dynamic random resistor network [5], postulates that the conductive backbone is perfectly linear but requires that each of these bonds which are non-conducting at low voltages becomes conductive when the voltage across it exceeds a critical value V_c. Such change in bond characteristics is considered to be reversible with application of low bias and can be regard as modeling in a reasonable manner the phenomenon of nonlinear hopping between dangling bonds across insulating regions in disordered mixtures.

The crossover current I_c and linear conductance Σ_1 fulfill the following scaling relationship:

$$I_c \sim \Sigma_1^x \tag{3}$$

where x is a critical exponent, directly related to dimension and to the type of models used to explain the nonlinearity of composites. However, the critical values, x, follows:

$$x \leq (\nu/t)(d-1) \quad \text{in the NLRRN} \tag{4}$$

$$x \leq 1 + \nu/t \quad \text{in the DRRN} \tag{5}$$

where ν is the correlation length critical exponent, d is the dimensionality of the composite and t is the critical percolation exponent in the classical percolation theory [1]. And the bounds [15], in three dimensions, have been established for x as

$$0.97 \leq x \leq 1.05 \quad \text{in the NLRRN} \tag{6}$$

$$x \leq 1.52 \quad \text{in the DRRN} \tag{7}$$

The limits on the values of x are valid when the exponent α satisfies the inequality:

$$1 < \alpha < \infty \tag{8}$$

4. Results and Discussion

4.1. Nonlinear conduction in HDPE/graphite nanosheets nanocomposites

The basic characteristics of nonlinear conduction are that the conductance of a given sample is no longer a constant and the I–V curves will not be a linear function of the applied voltage. Fig. 2 shows the several nonlinear I–V curves corresponding to HDPE/graphite nanosheets samples of different P (volume fraction) for small bias up to 2 V.

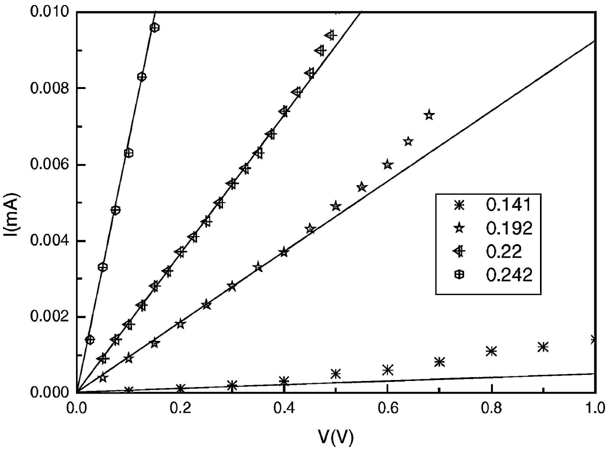

Figure 2 I–V characteristics of the HDPE/graphite nanosheets system with different graphite particles content. The straight lines correspond to the linear portions of the curves. (For clarity many points has been omitted.)

The curves, at small voltages, are linear, whereas they deviate from linearity and bend towards the current axis with increasing bias. Furthermore, it has been seen that I_c decrease as graphite nanosheets content decrease, namely, the closer one is to the percolation threshold, less current it takes to cause the onset of nonlinearity for a series of samples with same size. The enhancement of nonlinearity near p_c should be understood in the following way: since ξ diverges at p_c, the current across a conducting channel also increases remarkably as the percolation threshold is approached, thus causing enhancement of nonlinear conduction behavior in the vicinity of p_c, for $L<\xi$ (L is the sample size, ξ is correlation length).

The crossover points I_c, V_c may be thought as defining current and voltage scales for a sample corresponding to a given graphite nanosheets content. Fig. 3 reveals collapse of the I–V curves when plotted in scaled variables (for clarity, many data corresponding to some given graphite nanosheets content have been omitted). Apparently, data collapse only up to a certain point ($V/V_c \sim 1.7$) within the linear region. The divergence of curves beyond certain value of V/V_c implies that there may be another scale of current and voltage for any given sample. On the basis of the collapse of different I–V curves in Fig. 2, the relationship between I/I_c and V/V_c can be expressed as [9]:

$$I/I_c = \varphi(V/V_c) \tag{9}$$

where ϕ is a function independent of p. And for, $z \leq 1$, $\varphi(z) \approx z(z = V/V_c)$.

Interestingly, curves for some given samples, are smoothly varying within the range of measurements (type A, Fig. 4), however, other curves (type B, Fig. 5) exhibit several steps corresponding to sharp change in the sample

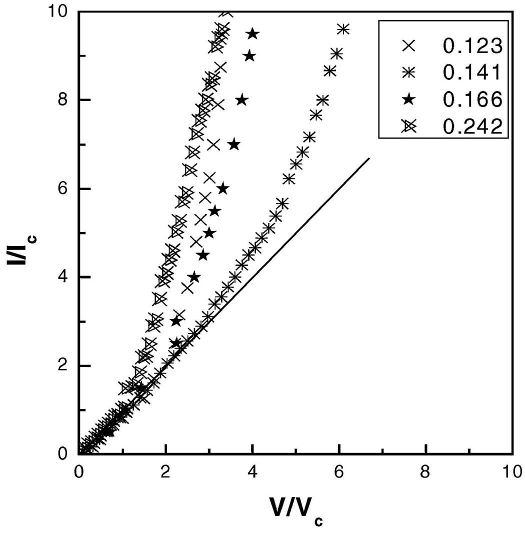

Figure 3 Scaled plots of the I–V curves. Data do not scale at high voltage.

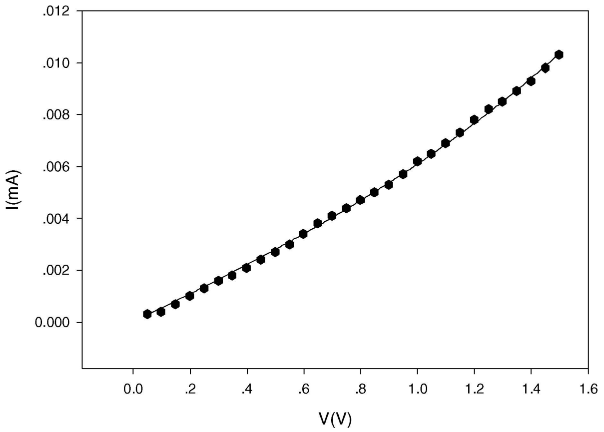

Figure 4 A smooth, nonlinear I–V curve (type A) of a sample with linear resistance 175 kΩ. The solid data is a fit to the data with $I = \Sigma_1 V + \Sigma_2 V^3$.

resistance. We will discuss these two types of nonlinear conduction [15] in detail.

A typical example of a smooth I–V characteristic is shown in Fig. 4. Surprisingly, the I–V curves are fitted well by a cubic term:

$$I = \Sigma_1 V + \Sigma_2 V^3 \tag{10}$$

where Σ_1 is the linear conduction and Σ_2 is the second order conduction. The fitted parameters are 5.7 $\mu\Omega^{-1}$ for Σ_1 and 0.7 $\mu\Omega^{-1}$ V^{-2} for Σ_2, corresponding to a linear resistance of 175 kΩ for the sample in Fig. 4.

The crossover current I_c scales as:

$$I_c \sim \Sigma_1^{b/(b-1)} \Sigma_2^{1/(1-b)} \tag{11}$$

based on the assumption that crossover to nonlinear occurs when two terms on right side of equation:

$$I = \Sigma_1 V + \Sigma_2 V^b \tag{12}$$

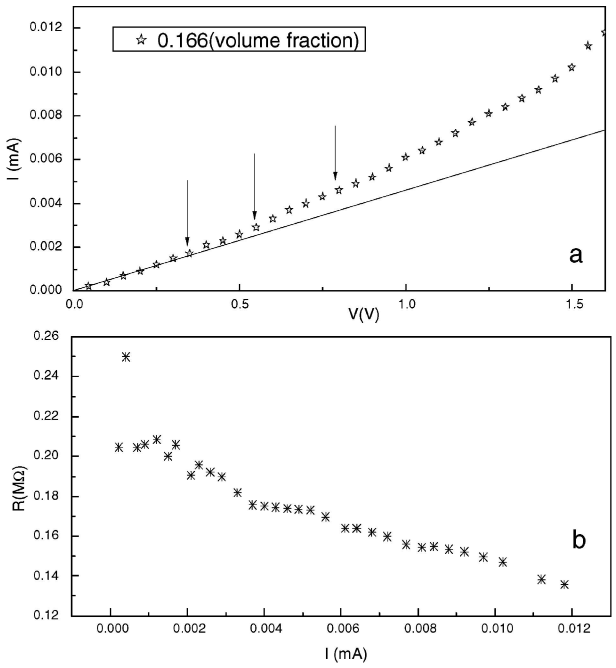

Figure 5 (a) An I–V characteristics (type B) with several steps marked by arrows. (b) Plot of *R* versus *I*.

become comparable in magnitude. Assuming that $\Sigma_2 \sim \Sigma_1^y$, the generalized form deduced from above relationships is given by [15]:

$$(b-1)x + y = b \tag{13}$$

If $y = 0$, namely, the scaling of Σ_2 is ignored, Eq. (11) will be reduced to the expression for x as proposed by Gefen *et al.* [5]. I_c and Σ_2 as a function of Σ_1 are displayed in Fig. 6. Exponents from the slope in Fig. 6 are:

$$x = 1.28 \pm 0.05, \quad y = 1.00 \pm 0.25$$

This is first determination of exponents x and y in HDPE/graphite nanosheets composites.

I–V characteristics (type B) of a sample are shown in Fig. 5. Apparently, the onset of nonlinearity is accompanied by small reversible steps in the current-voltage curves indicating sharp minimum in the resistance R. It should be pointed out that, considering that uncertainties in the measurements of V, the closer two consecutive values of currents are, the more uncertain R becomes. R–I curves obtained in the case are, actually, noisy. Since the points in current-voltage curve after a step jump as a whole parallel to the I axis to higher values of current, it is reasonable to assess that the structure of R–I curve is true and beyond error resulting from measurements. The first such step mentioned above corresponds to the onset of nonlinearity, marked by an arrow. There exists a second step at about $I \sim 3$ μA implying a drop in R. And the subsequent behavior of R exhibites mild drop, despite the appearance of minima. The structure of graphite nanosheets,

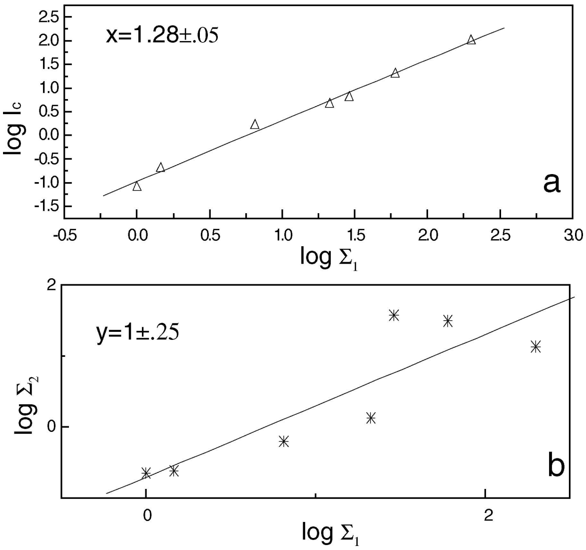

Figure 6 (a) Plot of crossover current, I_c, versus Σ_1 ($\mu\Omega^{-1}$) for two types of curves. (b) Plot of second-order conductance, Σ_2 ($\mu\Omega^{-1}$ V^{-2}), versus Σ_1 for two types of curves.

interfacial interaction between the graphite particles and HDPE may play an important role in yielding jumps. Chakrabarty *et al.* [15] concluded that morphological structure of conducting fillers should not be responsible for such steps in their case. However, whether these factors mentioned above may lead to such outstanding structure is to be substantiated.

4.2. Applicability of pertinent models to HDPE/graphite nanosheets composites

In this section, we will discuss which model can fully account for nonlinear conduction behavior of HDPE/graphite nanosheets composites.

Based on the NLRRN model, Chakrabarty *et al.* [14] derived the following inequality for exponents:

$$x \leq (\nu/y)(d-1) \tag{14}$$

$$y \geq 2-(\nu/t)(d-1) \tag{15}$$

In 3D, $x \leq 2(\nu/t) = 0.86$ and $y \geq 1.14$. The values are not in fair agreement with our experimental results in Fig. 6. Guohua Chen *et al.* [11] found that the values of x obtained fell into an approximately range of $1.10 \leq x \leq 1.30$, clearly incompatible with predictions of NLRRN model. Furthermore, Celzard *et al.* [16] proposed that $y \geq 0.95$ with $\nu \approx 0.89$ and $t \geq 1.7$. The bounds for x and y can be easily influenced by changing the values of ν and t and thus we can estimate that the values of x and y in real systems are non-universal.

Within DRRN model, it has been demonstrated that $x \leq 1 + \nu/t$. In three dimensions, $x \leq 1.43$, which is consistent with experimental results. However, the inequality becomes unpersuasive when the results based on the assumption of analytic properties of conductance as a function of voltage is taken into consideration. When the leading nonlinear term is V^b, the relationship between x and b can be shown by the following equation:

$$x = b(b-1) \tag{16}$$

For $b = 3$, in our case, $x = 1.5$. Disagreement with the value of x may occur. No expression for y in DRRN model, in addition, is available, although $y = 1.00$ is in fair agreement with the prediction of NLRRN model offered by Celzard *et al.* [16]. Abhijit *et al.* [17] suggested that one could not justify by fitting the I–V curve with a power-law and finding out the nonlinear exponent because that fitting was unpersuasive. One may consider to fit the nonlinear regime of an I–V curve with an nth degree polynomial function. In fact, an easy choice is fitting the experimental results with the power-law $I = \Sigma_1 V + \Sigma_2 V^b$, assuming that the leading nonlinear term is V^b (i.e., ignoring the high-order terms). Selection of the range of the I–V data for the purpose of the fitting may be responsible for the confusion that different experimental results were reported in the literature [17]. On the other hand, one may not know up to what voltage scale (in the nonlinear region) one should fit the data and thereby one may obtain various values of the exponents. As a result, prediction of classical models and experimental results are not in fair agreement.

It is not clear how to interpret the R–I curve in Fig. 5. Such structure, to our knowledge, has not been reported. Unfortunately, however, neither NLRRN nor DRRN can successfully explain this outstanding feature. In fact, there exists no microscopic mechanism of the DRRN model that may lead to the decrease of conductance, although simulation based on a 2D lattice found that the conductance as a function of applied bias increased monotonically [5]. It is likely that replacing resistors in model discussed above with conductive elements having complex behavior may account for such structure. But, whether macroscopic statistical properties of these conductive elements can result in this outstanding curve is yet to be determined.

4.3. Conduction mechanism

Nonlinearity in the HDPE/graphite nanosheets composites may arise from new conduction channels resulting from applied voltage [18–20]. In real mixtures, there may be open-ended loops between dangling clusters branching off the backbone and bridged by thin insulating media. Consequently, these transport behavior can be regarded as flow processes in a Cayley Tree (or a Bethe Lattice [1]) with junctions opened or closed at different values of applied voltage. Relatively wide distribution of connections can be facilitated by branched structure of the conductive backbone so that more connections are opened with increase of voltage and thus lead to macroscopic nonlinear conduction. Such dynamic processes are considered to be tunneling or hopping conduction processes.

We evaluate that the nonlinear conduction behavior of HDPE/graphite nanosheets composites may be explained well with a combination of NLRRN and DRRN, since neither of models can satisfactorily interpret nonlinear I–V characteristics in present case. The combined model, nonlinear random dynamic resistor network (NLRDRN) [21], is based on the fact that nonlinearity may originate from a combination of the amplication of nonlinear contribution of each element and the productions of new conducting channels with enough strong local fields. As a matter of fact, the particle–particle interaction of graphite may be nonlinear because the graphite nanosheets may be more or less coated by insulating HDPE films. The current passing through a channel increases remarkably, causing amplication of nonlinearity near P_c, for the conducting network becomes very tenuous and the number of conductive pathways becomes low as P tends towards P_c from above. On the other hand, intercluster and intracluster tunneling or hopping through insulating gaps can yield new conducting pathways causing supplementary nonliearity [17]. These are consistent with experimental results that nonliearity becomes more obvious as P_c is approached from above. However, detailed studies on the microscopic mechanisms causing macroscopic nonlinear conduction behavior of HDPE/graphite nanosheets composites will be complicated, although they are challenging and intriguing.

5. Conclusion

In conclusion, nonlinear I–V characteristics of HDPE/graphite nanosheets composites near the percolation threshold were studied. Two types of curves were observed. Some curves are smooth, while others display novel feature of sharp steps in I–V curves that needs further investigation. The exponent for critical current and the exponent for second-order conductance in two types of I–V curves have been found. However, two models, DRRN and NLRRN, cannot completely explain experimental results in present case. A successful model, applicable for experimental results, may account for why some structures are exhibited in some R–I curves, and absent in others. Such a model must consider the underlying microscopic dynamic processes directly related to structures in I–V curve. A combined model, NLRDRN, may semiqualitively explain the nonlinear conduction, although whether the applicability of it is to be determined.

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