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Conductivity critical exponents lower than the universal value in continuum percolation systems

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Abstract

A simple model was developed which explains how a continuum percolation system can attain a conductivity critical exponent, t, lower than the universal value. In this model, a structure parameter, κ, was developed to evaluate the geometry of the original conductor shape. Another parameter η accounts for the average backbone probability density $\langle M_B \rangle$ of the conductive phase within the percolation system. The structure parameter κ was used to evaluate the 'sensitivity' of the critical exponent t to the average backbone probability density $\langle M_B \rangle$. As $\langle M_B \rangle$ increased, a lower t could be obtained. To test this model experimentally, a Cu–Cu_2O conductor–insulator material was developed and tested. In this conductor–insulator material, C was used to reduce Cu_2O into Cu and CO, which produced a material with an optimum $\langle M_B \rangle$ and allowed the critical exponent $t = 0.87 \pm 0.1$ at $p_c = 0.23 \pm 0.01$ to be achieved.

The transport properties of a percolation system have received much attention around the world for several decades [1–4], because their comprehension is important for the understanding of the disordered systems. A major research challenge in a percolation system is the dc electrical conductivity. When the dc electrical conductivity, σ_{eff}, of a percolation system is measured as a function of the volume concentration p of the conducting phase, it follows a power law behavior of the form [5–8]:

$$\begin{aligned} \sigma_{\text{eff}} &\propto (p - p_c)^t, \qquad p > p_c \\ \sigma_{\text{eff}} &\propto (p_c - p)^{-s}, \qquad p < p_c \end{aligned} \tag{1}$$

where p_c is the percolation threshold, t and s are the electrical conductivity critical exponents above and below the percolation threshold, respectively. In 1980s, the values of the conductivity critical exponents of the percolation system were considered to be universal such that $t \approx 1.3$–1.4, $s \approx 0.5 (d = 2)$ and $t \approx 1.6$–2.0, $s \approx 0.6 (d = 3)$ based on renormalization group theory [8, 9], and in practical applications, they were generally considered to belong to the same universality class as the corresponding lattice percolation problems [10]. However, some experimental and numerical results have indicated that the lattice percolation problems and the practical application problems may belong to different universality classes [10–14]. In past research, several groups measured that the critical exponent was in good agreement with the universal value of $t = 2.0$ for various disordered conductor–insulator composites [15–18], while others measured that the critical exponent was larger than the universal value [13, 15, 19]. With the mean-field type argument, Kogut and Straley (KS) [20] first realized that if the low-conductance bonds in percolation resistor networks were characterized by a certain form of anomalous conductivity distribution, then the universality of the conductivity exponents would be broken. In their model, by assigning to each neighboring pair in a regular lattice, a bond with finite conductivity g with probability p and zero conductivity with probability $1 - p$, the resulting bond conductivity distribution function becomes:

$$\rho(g) = ph(g) + (1 - p)\delta(g) \tag{2}$$

where $\delta(g)$ is the Dirac delta function and $h(g)$ is the distribution function of the finite bond conductivities. If $h(g)$ has a power law divergence for small g of the form

$$\lim_{g \to 0} \propto g^{-\alpha} \tag{3}$$

where $\alpha \leqslant 1$, then the universality is lost for sufficiently large values of exponent α.

Based on the KS model, two models have been developed to explain the non-universality of the critical exponent in

percolation systems, known as the 'Random Void' model (Swiss–Cheese model) where the voids between the particles carry the current [11, 12]; and the 'tunneling' model where the resistance between adjacent particles is determined by a tunneling process [21–23]. Conductor–insulator systems, such as granular metals (or metal-oxides) and carbon black-polymer composites are well explained by the random void and tunneling models, respectively. However, in both random void and tunneling models the conductors are both spherical and these two models are not able to describe the percolation system with non-spherical conductors. Therefore, one has to come up with a model for a possible non-universal behavior in the conductor–insulator composite system. In recent years, plenty of attention has been focused on the utility of the 'percolation backbone' to demonstrate the real path that carries the current. In a percolation system, the percolation cluster can be decomposed into two categories: the 'backbone' and 'dangling ends' [10] that show different properties.

Although the non-universality of physical properties in percolation systems was presented about thirty years ago, the discrepancy between the numerous experimental results and the corresponding available theories still remains incompletely understood. For the vast majority of these cases, the critical exponent was not found to be lower than the universal value [24, 25], and to our knowledge, there are no theories that explicitly deal with the electrical conductivity critical exponent lower than the universal value. In this study, we would like to give a simple model with two key probability densities: the backbone density M_B and the dangling ends density M_D as the parameters. The backbone (dangling ends) density is defined as the total backbone (dangling ends) proportion belongs to the percolation infinite clusters. We also suggest a new system, C reduced Cu/Cu_2O cermet, in which a conductivity critical exponent less than the universal value is predicted and observed.

In order to realize a critical exponent lower than the universal value, the conductance between two randomly selected particles (or nodes), g, is given by

$$g = g_0 e^{-\kappa M_D/M_B} \tag{4}$$

where g_0 is a constant, M_D and M_B are dangling ends and backbone densities belong to two randomly selected particles, and κ is an ad hoc 'structure parameter', which represents the geometry and topology structure of the conductor. In a real conductor–insulator percolation system, the value of κ will reach its highest value when the geometrical shape of the original conductor is spherical, because a sphere is the simplest geometrical shape. The value of κ will decrease with increasing geometrical complexity of the conductor. In this equation, the tunneling conductance parts should be considered as a part of the backbone. In order to find the conduction distribution function of the network $H(M_D/M_B)$, one must give the distribution function of the dangling ends and the backbone. In this case, the dangling ends and backbone distribution function is given by:

$$H(M_D/M_B) \propto \frac{\eta^2 M_D}{M_B} \exp\left(-\frac{\eta M_D}{M_B}\right) \tag{5}$$

where η is the average value of M_B/M_D written as $\eta = \langle M_B/M_D \rangle$. In a real percolation network, this value is decided by the structure of the backbone and the dangling ends. It will achieve its maximum value with the 'highest-structure' of the conductor, because most of the 'arms' [21] in the aggregates get entangled each other. Equation (5) will peak at $\eta = M_B/M_D$, and the distribution width is also decided by M_B/M_D. The general relationship between these two distribution functions can be written as [23]:

$$f(g) = H(M_D/M_B)\frac{d(M_D/M_B)}{dg} \tag{6}$$

using equations (4)–(6), it can be written as:

$$f(g) \propto [\ln(g/g_0)]g^{(\frac{\eta}{\kappa}-1)} \tag{7}$$

for small g values, it can be deduced

$$g^{(\frac{\eta}{\kappa}-1)} = g^{-\alpha} \tag{8}$$

following the above equations, the exponent α is given by:

$$\alpha = 1 - \frac{\eta}{\kappa} \tag{9}$$

thus, combined with Kogut and Straley's model [20]

$$t = t_{un} + \frac{\alpha}{1-\alpha} \tag{10}$$

the critical exponent t can be expressed as:

$$t = t_{un} + \frac{\kappa}{\eta} - 1 = t_{un} + \kappa\left\langle\frac{M_D}{M_B}\right\rangle - 1 \tag{11}$$

where t_{un} is the accepted universal value of the critical exponent.

In equation (11), if the backbone contribution to the conductivity is higher than the dangling ends contribution, a t value less than the universal value can be realized. With equations (1) and (11), it can be seen that the electrical conductivity is not just dependent on the backbone density, but also on the 'structure factor' κ. This phenomenon has already been proved by Paul [26], that the 'shortest path' between two randomly chosen particles is not the same even with the same backbone density. Figure 1 gives the simulated results of the critical exponent t as a function of average backbone density $\langle M_B \rangle$ with different κ values. It is clear that the critical exponent t decreases with increasing backbone density $\langle M_B \rangle$ for fixed κ value. The value of κ is decided by the structure of the backbone, and it represents the 'sensitivity' of the critical exponent to the average backbone density $\langle M_B \rangle$. In figure 1, it can be seen that the t value becomes more and more sensitive to $\langle M_B \rangle$ with increasing κ value[1].

According to Balberg's description [21], the structure of the conductor can be divided into 'high-structure' and 'low-structure'. The larger and complicated aggregates are usually called 'high-structure', while the smaller and geometrically simpler aggregates are called 'low-structure'. The universal, or the lowest value of the conductivity exponent, can be

[1] The decision of the detailed value of t will be discussed in our future work.

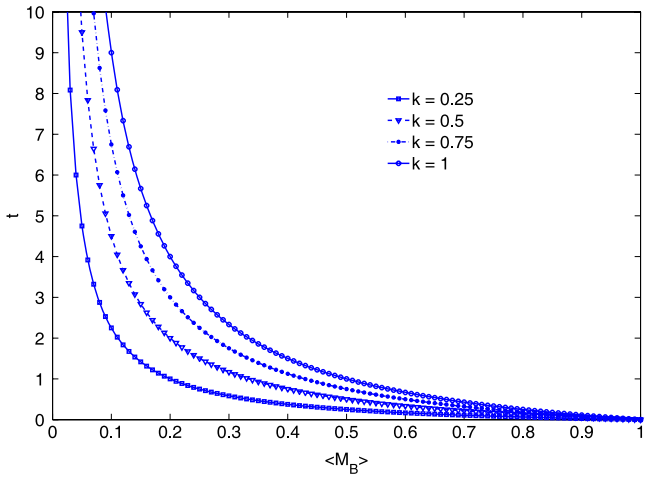

Figure 1. Critical exponent t as a function of average backbone density $\langle M_B \rangle$.

(This figure is in colour only in the electronic version)

achieved with the 'highest-structure' because the 'arms' of the 'high-structure' conductor entangle while the centers still form a random distribution. According to his argument, it can be deduced that more backbone can be formed in the 'high-structure' conductor percolation system than in the 'low-structure' percolation system. However, it is still not clear how the structure of the conductor is defined as the 'highest', and how to make the structure of the conductor higher. In prior research results, both from experiments and computer simulations, most of the mass of the infinite network at the threshold belongs to the dangling ends, not to the backbone [27]. Thus, most of the mass contained in p makes no contribution to the conductivity g, and as noted, only the backbone contributes to the conductivity of the cluster. In a percolation system, the backbone structure is complicated. The main roads are composed by links and blobs, and all of the links and blobs have their dangling ends. Therefore the conductivity critical exponent differs with different conductor–insulator materials due to the different density of the backbone and the dangling ends. Due to the critical exponent t is a function of α, and α is a function of η, which depends on the backbone density of the conductor, it can be deduced that the higher the average backbone density of the conductor, the higher the η value and the lower the critical exponent of the system will be. If considered from the geometrical and topological aspect, it is not very hard to find that the more complex the conductor's geometrical shape, the easier for them to connect each other, which increases the probability of forming a backbone and increasing the backbone density. Thus, it brings us back to the question how can we make the backbone density of the conductor higher to increase the η value, and thus obtain a relatively low conductivity critical exponent?

To obtain a high backbone density in a real percolation conductor–insulator system, electrical conductivity studies were performed on a Cu/Cu_2O cermet composite made via a C reduction method. High purity Cu_2O and C powders were used to prepare this insulator–conductor composite. The average particle size of Cu_2O was about 10 μm, and C was in the form of 100–200 nm diameter spherical agglomerates. Powders were ball-milled in dehydrated ethyl alcohol for 12 h, and subsequently dried in a furnace at 80 °C. After drying, the mixture powders were heated in a graphite die to 650 °C (20 °C min^{-1}, no pressure, 60 min soak) followed by heating to 1050 °C (20 °C min^{-1}, 25 MPa pressure, 40 min soak). The furnace chamber was purged with 1.0 atm of argon gas from the start of the hot pressing procedure. After HP processing, the relative density of the final materials were measured to be higher than 98%.

The reduction procedure is very complicated [28] because there will be CO produced during this procedure, and CO will reduce the Cu_2O matrix into Cu. In the final stage, C will be oxidized into CO_2, and the content of the conductor Cu, which was reduced by the C, can be calculated by the following reaction:

$$C + 2Cu_2O = 4Cu + CO_2\uparrow. \qquad (12)$$

Specimens were cut into the shape of bar with a size of 10 mm × 10 mm × 30 mm, and all results were obtained at room temperature. Four platinum wire electrodes were wrapped around the cermet samples and non-fluxed platinum paste was painted to decrease the contact resistance. The dc electrical conductivity of the composites was measured with a 4-probe technique [13, 15, 24].

In order to find the conductivity exponent, the conventional three parameters, p_c, t, and σ_0 were used. In figure 2(a), the room temperature electrical conductivity $\lg \sigma_0$ as a function of the Cu_2O volume concentration p is shown, and the same data are demonstrated as a log–log plot in figure 2(b). As can be seen from this figure, the conductivity data follow the power law behavior of equation (1) with percolation threshold $p_c = 0.23 \pm 0.01$, and the fitted value of the critical exponent $t = 0.87 \pm 0.1$, which is lower than the universal value, was calculated with least-square method. In this system, there are no oxide coatings between the tightly compressed and amorphous metal grains, and tunneling cannot occur along the current carrying backbones of this C reduced Cu/Cu_2O cermet system; thus, the situation can not be mapped onto the tunneling model in this system. Meanwhile, the structure of the conductor is not spherical; hence, the random void model is not applicable in this system either. Therefore, we use the backbone density to give an explanation of the low t value.

In a percolation network, according to equation (1), the conductivity critical exponent depends on σ_{eff} and p, and the backbone structure solely determines the conductivity of the whole system [29]. In past research, a higher backbone density was realized by increasing the conductor concentration, which means the contribution of the increasing effective conductivity came from the 'extra' conductor concentration. Hence, according to equation (1), the critical exponent is not able to achieve a value lower than the 'universal value' because of the increasing conductor concentration p. In order to decrease the t value, the effective electrical conductivity must be increased but without increasing the conductor concentration p. It was considered by Macheta [30] that the effective electrical conductivity of a percolation system depends only on the links of the backbone, and the conductivity contribution of the blobs

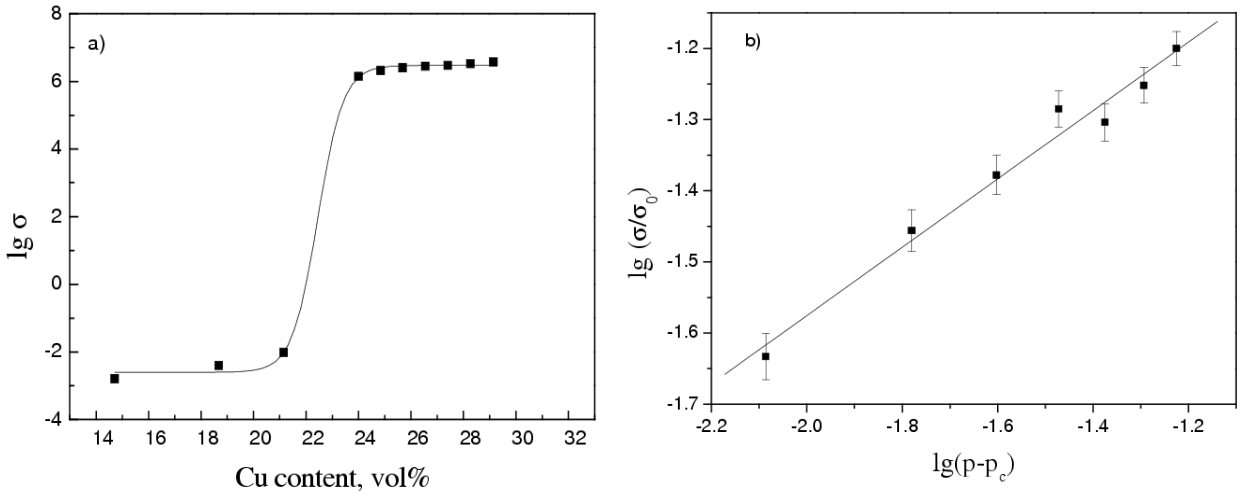

Figure 2. (a) Conductivity as a function of volume concentration p for C reduced Cu/Cu_2O cermet. (b) Log–log plot of the same data with fits to equation (1).

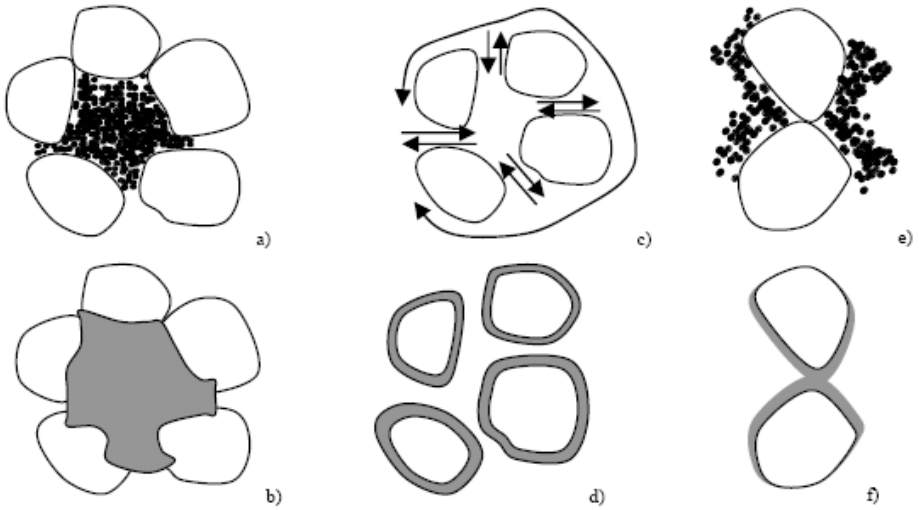

Figure 3. Schematic diagram of three categories of conductor structure of the C reduced Cu_2O /Cu cermet. The black dots represent the agglomerates of C, the circles near them represent the Cu_2O matrix, the arrows represent the CO flow, and the gray areas represent the reduced conductor Cu. (a) and (b) represent the C reduced nearest contacted Cu_2O particles before and after the reduction process; (c) and (d) represent the CO reduced surfaces where it passes through before and after the reduction process; (e) and (f) represent the C and CO reduced thin neck of the Cu_2O matrix before and after the reduction process.

is irrelevant by using a hierarchical model for the backbone. However, Alava proved that the blobs determine the critical transport properties by finding the *maximum flow* of current [29].

In this C reduced C/Cu_2O cermet system, the conductor Cu was not just reduced by C but also by the CO which was produced by the reduction of CO_2. Therefore, the structure of the conductor did not just depend on C concentration, but also depended on the flow of CO in the system. As CO was flowing through the matrix, the surfaces of the matrix particles were reduced into conductors. In addition, due to the diffusion effect, C or CO will 'penetrate' part of the necks of the matrix from one side to the other side to reduce the insulator necks into conductor paths. Hence, the structure of the conductor Cu was composed of three categories: firstly, the C reduced the nearest contacted Cu_2O particles; secondly, the CO reduced the surfaces where it passed through; and thirdly, C and CO reduced the thin necks of the Cu_2O matrix. In these three categories, the first one is the same as the former experimental conductor backbone structures, but the second and the third ones changed the backbone structure considerably. Due to the fluidity of the CO, the resultant structure produced is more flexible than the one produced by solid conductors directly. CO is able to fill into tighter spaces, therefore, the current flow paths or backbone density will be increased. In the third category, the thin necks of the matrix will be 'penetrated' because of the reduction, which leads to the connection of the non-connection agglomerates. Figure 3 gives the schematic diagram of the three reduction categories. In this system, each center of the C concentration can be considered as a Cayley tree

center. Although there are no loops in one Cayley tree [31], the '*Cayley trees*' still have a probability to connect with each other and form blobs. By this method, more 'arms' of the conductors will entangled because the air acts as a fluid, consequently, it can fill in small areas where the solid can not, and therefore, more links and blobs will be formed in the final network, and allow the conductor concentration to be more 'effective' to the conductivity contribution.

In summary, we have used a simple percolation model with structure parameter κ, dangling ends, and backbone densities to study the possibility of attaining a conductivity critical exponent t lower than the universal value. Our results show that the conductivity critical exponent t decreases with increasing average backbone density. The backbone density, which is governed by the structure parameter density is different with different structures of the conductor, which are governed by the structure parameter κ, changes with respect to different conductor structures. We designed a conductor–insulator percolation material using C to reduce the Cu_2O matrix into Cu, to realize a low t value in a conductor–insulator system. The experimental results show that the percolation threshold $p_c = 0.23 \pm 0.01$, and the critical exponent $t = 0.87 \pm 0.1$.

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