

A model for modified electrode with carbon nanotube composites using percolation theory in fractal space

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ABSTRAC

We introduce a model for prediction the behavior of electrodes which modified with carbon nanotubes in a polymer medium. These kinds of polymer composites are developed in recent years, and experimental data for its percolation threshold is available. We construct a model based on percolation theory and fractal dimensions and using experimental percolation threshold for calculating the moments of current distribution function.

Keywords: Modeling of modified electrode; Percolation theory; Fractal space; Carbon nanotubes

INTRODUCTION

Carbon nanotubes are the most exciting new materials to have been discovered in the past 30 years. The explosion of interest in carbon nanotubes can be traced back to a 1991 Nature paper by Sumio Iijima [1]. The structures discovered by Iijima were far more perfect than any that had been seen before, and promised to have exceptional properties. Carbon nanotubes are excellent electrical conductors [2], with current densities of up to 10^{11} A m⁻², and have very high thermal conductivities [3]. Many of these properties can be best exploited by incorporating the nanotubes into some form of matrix, and the preparation of nanotube containing composite materials is now a rapidly growing subject [4, 5]. Multiple applications are expected for nanocomposite materials and therefore many

research works are currently devoted to their incorporation into a metal, ceramic or, more commonly, polymer matrix. The composites are generally prepared by mixing the desired quantity of single- or multi-walled carbon nanotubes with the matrix, which is either dissolved or in suspension in a liquid medium, before further treatments. One of the most important properties of nanocomposite materials is conductivity, and many researches, work on electrical percolation of carbon nanotubes in polymer composites [6]. *Percolation threshold* was experimentally measured for many kinds of carbon nanotubes and polymer matrixes. In this paper we want to introduce a model based on percolation theory in fractal space for prediction of electrical behavior of modified electrodes with carbon nanotube composite polymers.

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Percolation theory:

Percolation processes were first developed by Flory (1941) and Stockmayer (1943) to describe how small branching molecules react and form very large macromolecules [7]. In 1957, Broadbent and Hammersley introduced percolation theory, as a stochastic way of modeling the flow of a fluid or gas through a porous medium of small channels which may or may not let gas or fluid pass [9]. The terms fluid and medium were viewed as totally general: a fluid can be liquid, vapor, heat flux, electric current, infection, a solar system, and so on. The medium can be the pore space of rock, an array of trees, or the universe. It is very important that we attend to the difference between diffusion process and percolation process, in the first case fluid particles decide where to go in the medium, but in the second case the medium dictates the paths of particles.

We can define percolation theory as a general mathematical theory of connectivity and transport in geometrically complex systems [10]. The remarkable thing is that many results can often be represented in a small number of simple algebraic relationships.

Percolation theory is classified in two kinds, *site percolation* and *bond percolation*. In the first kind we have an infinite lattice of sites which may occupied with probability p or unoccupied with probability $1-p$. In the other kind an infinite lattice of bonds exist and each bond may closed with probability p and open with $1-p$. A set of sites (or bonds) that connected to each other makes a cluster, and in a lattice, one can find different kind of clusters in shape and size. It is clear that if p increases then the mean cluster size grow up and in a particular probability we envisage with an infinite spanning cluster which connected two side of the lattice (percolation done). This particular probability is phase

transition threshold of system that it was introduced as *percolation threshold* p_c . This

quantity relates only on geometry of lattice, and it was calculated for much kind of lattices (some with exact calculation and others with computer simulation) [7, 8].

In addition to the percolation threshold, the topological properties of percolation networks are characterized by several important quantities, like as percolation probability $P(p)$, mass of infinite cluster $M(p)$, backbone mass $M_B(p)$, correlation length $\xi(p)$, average number of clusters with size s , $n_s(p)$, mean cluster size $S(p)$, effective conductivity $g(p)$, and so on. The value of every percolation quantities for any p depends on the microscopic details of the system. But near the percolation threshold, most of these quantities obey scaling laws that are largely insensitive to the network structure. For example near p_c we have the following scaling laws:

$$\begin{aligned} P(p) &\propto (p - p_c)^\beta \\ M(p) &\propto (p - p_c)^\beta \\ M_B(p) &\propto (p - p_c)^{\beta_B} \\ \xi(p) &\propto |p - p_c|^{-\nu} \\ S(p) &\propto |p - p_c|^{-\gamma} \\ g(p) &\propto (p - p_c)^\mu \end{aligned} \quad (1)$$

The exponent's β , β_B , ν and γ are completely universal. It means that they have not any relation to the microscopic details of the system and depends only on the dimensionality of the system. The exponent μ is one of the transport exponents in percolating systems, and it also largely universal. So if one knows the dimension of a system then can find the universal exponent's and vice versa.

Fractals in percolating systems:

It is not easy to obtain many exact analytical results for cluster properties, and most of our knowledge come from complex numerical calculations. In such cases it is very useful to

invent simple mathematical model, on which we can do analytical calculations. It was clear that the geometry of infinite cluster at p_c is fractal [11]. Benoit Mandelbrot introduced fractal geometry as a unifying description of natural phenomena which are not uniform but still obey simple power laws of the form

$$M \propto L^D \quad (2)$$

D is non-integer dimension and L is linear size of system. Fractal dimension describe subset of the cluster sites (or bonds) necessary for calculating different cluster properties. The formal mathematical definition of fractal is defined by Benoit Mandelbrot. It says that a fractal is a set for which the Hausdorff Besicovich dimension strictly exceeds the topological dimension [11]. However, this is a very abstract definition. Generally, we can define a fractal as a rough or fragmented geometric shape that can be subdivided in parts, each of which is (at least approximately) a reduced-size copy of the whole. Fractals are generally self-similar and independent of scale.

THE MODEL

The calculation of critical exponents in equation (1) shows that there is no distinguish between different type of two-dimensional lattice, such as square, triangular or honeycomb lattice. The same is true for d-dimensional lattices. Also, bond and site percolation have the same exponents. All evidence suggests that the critical exponents depend only on dimensionality of the lattice, and they are *universal* [7]. Critical exponents were exactly calculated for Bethe lattice, in which each site is connected to z nearest neighbors in a way that no closed loops are possible and percolation threshold is $p_c = (z-1)^{-1}$. One of the important exponents that appears in the scaling law of conductivity is μ , and for Bethe lattices $\mu=3$. The values of the critical exponents obtained for the Bethe lattice are the limiting case when the dimensionality of the system goes to infinity. The accurate studies show that the Bethe

lattice critical exponent values are exact at $d \geq 6$, but in less dimensions it is identified with an expansion factor (ε) as follow:

$$\mu = 3 - (5\varepsilon/21) \quad (3)$$

On the other hand, if we purpose that the geometry of infinite cluster at p_c is fractal (so subsets of this cluster are fractal), then it is possible to determine the fractal dimension of this cluster (and its subsets) in term of ε :

$$D = 4 - (10\varepsilon/21) \quad (4)$$

$$D_B = 2 + (\varepsilon/21) \quad (5)$$

$$D_{\min} = 2 - (\varepsilon/6) \quad (6)$$

$$D_{\max} = 2 - (\varepsilon/42) \quad (7)$$

In these equation, D , D_B , D_{\min} and D_{\max} are the fractal dimension of infinite cluster, backbone, minimal path (chemical distance), and maximal self avoiding path respectively. Backbone is a set of clusters that they are connected to each other by a single bond and connects the opposite edges. It means there is practically only one chain of bonds in infinite cluster that connects two sides of the system. One can find the shortest way in backbone, it is minimal path. Also, the longest way in backbone is named as maximal self-avoiding path. With respects to relation between critical exponents and expansion factor (3), and the relations between fractal dimensions and expansion factor (4 to 7), we expect that the fractal dimensions and critical exponents are directly related to each other.

$$D = 2\mu - 2 \quad (8)$$

$$D_B = (13 - \mu)/5 \quad (9)$$

$$D_{\min} = (7\mu - 1)/10 \quad (10)$$

$$D_{\max} = (\mu + 17)/10 \quad (11)$$

Now we can construct a fractal space and expand our system in such environment. Mandelbrot and Given proposed the recursive construction shown in Fig. 1: one begins with a straight segment of unit length, and at each iteration it is replaced by eight segments [12].

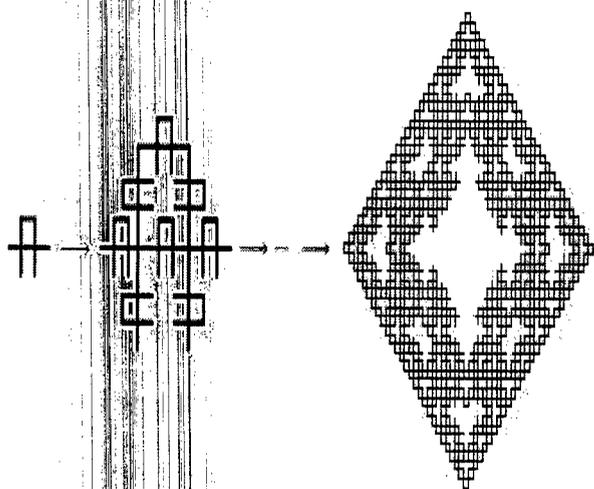


Fig.1 Mandelbrot curve generation.

The length scale changes by a factor b which named generalized rescale factor. The generalized Mandelbrot-Given curve has L_1 singly connected bonds, L_2+L_3 bonds in the blob (with $L_2 \leq L_3$), and L_4 dangling bonds and they have relations with fractal dimensions as follow:

$$D = \log(L_1 + L_2 + L_3 + L_4) / \log b \quad (12)$$

$$D_B = \log(L_1 + L_2 + L_3) / \log b \quad (13)$$

$$D_{\min} = \log(L_1 + L_2) / \log b \quad (14)$$

$$D_{\max} = \log(L_1 + L_3) / \log b \quad (15)$$

A simple calculation shows that the fractal dimensions are able to explain the Mandelbrot-Given curve parameters (L_1 to L_4):

$$L_1 = b^{D_{\max}} - b^{D_B} + b^{D_{\min}} \quad (16)$$

$$L_2 = b^{D_B} - b^{D_{\max}} \quad (17)$$

$$L_3 = b^{D_B} - b^{D_{\min}} \quad (18)$$

$$L_4 = b^D - b^{D_B} \quad (19)$$

In a carbon nanotube-polymer composite, we can see a network of conductive parts which is distributed in a nonconductive medium, and also we can study the distribution of these particles with aim of distribution function. It is often convenient to calculate the moments of distribution function. The distribution or current in a random network is *multifractal* and therefore:

$$\frac{M_q(L)}{M_0(L)} = \sum_j \left(\frac{I_j}{I}\right)^{2q} = L^{\psi(q)} \quad (20)$$

In this equation $M_q(L)$, I_j , I and $\psi(q)$ are the q th moment of current distribution function, current through the bond j , total current and multifractal exponent respectively. The concept of *multifractality*, implies that $\psi(q)$ has not a linear relation with q .

If it is supposed that the network of carbon-nanotubes is a random network (it is necessary for applying the percolation theory), and this network has a structure like Mandelbrot-Given curve, we will be able to predict the moments of current distribution function. Blumenfeld *et al.* (1986) found that the multifractal exponents for the current distribution in such curve are given by:

$$\psi(q) = \frac{\log[L_1 + (L_2 L_3^{2q} + L_3 L_2^{2q}) / (L_2 + L_3)^{2q}]}{\log b} \quad (21)$$

Our model is based on calculating the Mandelbrot-Given curve parameters with respect to fractal dimensions of infinite cluster in a carbon-nanotube matrix (eqs.16-19) and then applies these parameters for prediction of $\psi(q)$ in eq.21. In order to compute the fractal dimensions, the experimental results of critical exponent of conductivity are applied (eqs.8-11).

RESULT AND DISCUSSION

There is one point about dangling bonds and its role in limitation of model. It is clear that the upper limit for our model is the Bethe lattice, in which we have infinite dimension and $\mu=3$. On the other side, calculation of dangling bonds in Mandelbrot-Given curve shows us the lower limit of model.

$$\frac{23}{11} \leq \mu \leq 3 \quad (22)$$

With applying the model in above limit, and according to experimental data, the first and second moment of current distribution function in an electrode which modified with carbon nanotube-polymer composite, was computed. The experimental critical

exponents of conductivity for some composites are collected in table.1 [14-21].

Table1.Experimental data for p_c and μ . (SWCNT=single wall carbon nanotube, MWCNT=multi wall carbon nanotube, PANI=polyaniline, PE=polyethylene, MA=poly methyl methacrylate, PAT=polyhexadecyl thiophene, PC=polycarbonate, PU=polyurethane)

	matrix	filler	aspect ratio	p_c (vol. %)	μ	Ref.
1	PANI	SWCNT	—	0.3	2.1	[16]
2	PE	SWCNT	—	0.25	2.2	[19]
3	PMMA	MWCNT	—	0.2	2.3	[20]
4	Epoxy	SWCNT	—	1	2.4	[15]
5	—	—	—	—	2.5	—
6	PAT	MWCNT	>200	12	2.6	[17]
7	Epoxy	SWCNT	400	0.005	2.7	[13]
8	PC	SWCNT	—	0.1	2.8	[18]
9	Epoxy	MWCNT	100	0.6	2.9	[14]
10	PU	MWCNT	>100	1	3	[21]

The fractal dimensions of backbone and its subsets are listed in table.2. And finally the generalized Mandelbrot-Given curve parameters and $\psi(0)$, $\psi(1)$ and $\psi(2)$ are given in table.3. It is seen that the exponent for zero'th moment of distribution function is equal to backbone fractal dimension (it was expectable). With deliberation on $\psi(1)$, it will be cleared that the model predict a logical relation between current and conductivity and it seems that the system sensitivity on current, increases with μ . Also $\psi(2)$ is a scale of deviation around average current, and the model tell us the fluctuation of current increase with μ more rapid than average current.

These moments of current distribution function, may be used for calculation of other properties of electrode that they relate to current. For example the exchange current density (i_0) is a very important quantity for investigation of electrode reaction kinetics.

On the other hand the current density can be controlled with applying different kinds of

composite in the surface of electrode or different concentrations of nanotube in composite and it means that it is possible (at least in this model) to control the kinetic of reaction. It may be the subject of further studies on this model.

The curve which we used for construction of fractal space is Mandelbrot-Given curve. There is many other curves can be used for this propose. One can study the effect of these curves and make a fractal space with better compatibility.

Table 2. Fractal dimensions as a function of μ

μ	D	D_B	D_{min}	D_{max}
2.1	2.2	2.18	1.37	1.91
2.2	2.4	2.16	1.44	1.92
2.3	2.6	2.14	1.51	1.93
2.4	2.8	2.12	1.58	1.94
2.5	3	2.1	1.65	1.95
2.6	3.2	2.08	1.72	1.96
2.7	3.4	2.06	1.79	1.97
2.8	3.6	2.04	1.86	1.98
2.9	3.8	2.02	1.93	1.99
3	4	2	2	2

Table 3. Generalized Mandelbrot-Given parameters and the moments of current distribution function.

μ	L_1	L_2	L_3	L_4	$\psi(0)$	$\psi(1)$	$\psi(2)$
2.1	1.68938	2.815219	6.463323	0.243657	2.18	1.178618	0.79954
2.2	2.377887	2.486797	5.864876	3.23705	2.16	1.289696	1.008681
2.3	3.090992	2.16256	5.242826	6.90226	2.14	1.393425	1.184085
2.4	3.831121	1.842385	4.594758	11.40576	2.12	1.491206	1.33616
2.5	4.60088	1.526151	3.918078	16.95489	2.1	1.584115	1.471227
2.6	5.40307	1.213738	3.209994	23.80793	2.08	1.672996	1.593418
2.7	6.240707	0.90503	2.467503	32.28659	2.06	1.758525	1.705584
2.8	7.117035	0.599913	1.687372	42.7916	2.04	1.841249	1.809778
2.9	8.035546	0.298273	0.866121	55.82213	2.02	1.921616	1.907527
3	9	0	0	72	2	∞	∞

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