Fractal Model for the ac Response of a Rough Interface

S. H. Liu
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
(Received 26 December 1984)

A fractal model is proposed for a rough interface between two materials of very different conductivities, e.g., an electrode and an electrolyte. The equivalent circuit of the model, which takes into consideration the resistance in the two substances and the capacitance of the interface, has the property of the so-called constant-phase-angle element, i.e., a passive circuit element whose complex impedance has a power-law singularity at low frequencies. The exponent of the frequency dependence is related to the fractal dimension. The model also provides insight into the conducting properties of the percolating cluster and the source of the $1/f$ noise in electronic components.

PACS numbers: 73.40.Mr, 73.25.+i

The transfer of electric charge across the interface between two substances is an ubiquitous process in modern technology. The process plays an important role in the case where the two substances are very dissimilar, e.g., a metal electrode and an aqueous or solid electrolyte. Physically, the electric current encounters Ohmic resistance in both substances and a capacitance across the interface. In reality, however, such an RC circuit does not give an adequate description of the ac response of the interface. It is found necessary to include a constant-phase-angle (CPA) element whose impedance has the form $Z \propto (j\omega)^{-\eta}$, where ω is the angular frequency, $j=\sqrt{-i}$, and $0<\eta<1$.[1] In recent years it has been demonstrated by many authors that the parameter η is intimately related to surface roughness, with η approaching unity when the surface is made increasingly smooth.[2-4]

Polished surfaces usually show long lines of scratches under magnification. Efforts have been made to model these grooves as distributed RC elements.[2,3] In many cases such elements can be reduced to an RC transmission line, which is a CPA element with $\eta=\frac{1}{2}$. Recently, Le Mehaute and Crepy have suggested that general fractional values of η arise from the fractal nature of the interface,[5] i.e., the geometrical property that a rough surface is self-similar under a scale transformation.[6] Their argument is intuitively appealing, but their attempt to derive a new diffusion equation with fractional-order time differentiation is not well justified.

The present paper derives a rigorous connection between a fractal model of a rough interface and the nature of the corresponding CPA element. The exponent is $\eta=1-\bar{d}$, where the fractal dimension $\bar{d}$ is to be defined later. Since η and $\bar{d}$ can be measured independently, a verifiable link is found between the surface roughness and the mysterious CPA element.

The cross section of the model interface is depicted in Fig. 1 in which the electrolyte side is shown in black. The grooves in the electrode are seen as protrusions on the electrolyte side. Each groove has the self-similar structure in that it subdivides into two branches, and the branches are similar to the whole groove when magnified by a factor a, $a>2$. The reader may recognize this model as the Cantor bar,[6] whose fractal dimension is calculated from the reduction of substance at each step, rather than from the length of the border under different scales. Viewed from the electrolyte side, the interface has the fractal dimension $\bar{d}=\ln 2/\ln a<1$. The model may be readily generalized to N grooves, each of which subdivides into N branches at every level. The scale factor a for self-similarity satisfies $a>N$ and $\bar{d}=\ln N/\ln a<1$. The length of the border has the fractal dimension $1+\bar{d}$.

The electric circuit analog of the interface in Fig. 1 is shown in Fig. 2. The resistance R increases by the ratio a at every stage of branching because of the reduction in cross-sectional area. The capacitance C, which is the same at every stage, actually represents the interfacial capacitance of the two lateral faces of the branch. The interfacial capacitance in the dip between branches becomes decreasingly important at higher branching stages, and can be shown to be an irrelevant parameter, i.e., it does not affect the impedance of the interface at low frequencies. The common ground is the electrode. The quantity R measures the difference in resistance between the electrolyte and the electrode; the latter is quite negligible.

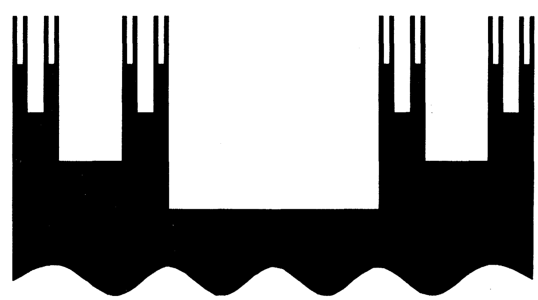

FIG. 1. Cantor-bar model of a rough interface between an electrolyte (black) and an electrode (white). Two grooves each with four stages of branching are shown.

© 1985 The American Physical Society

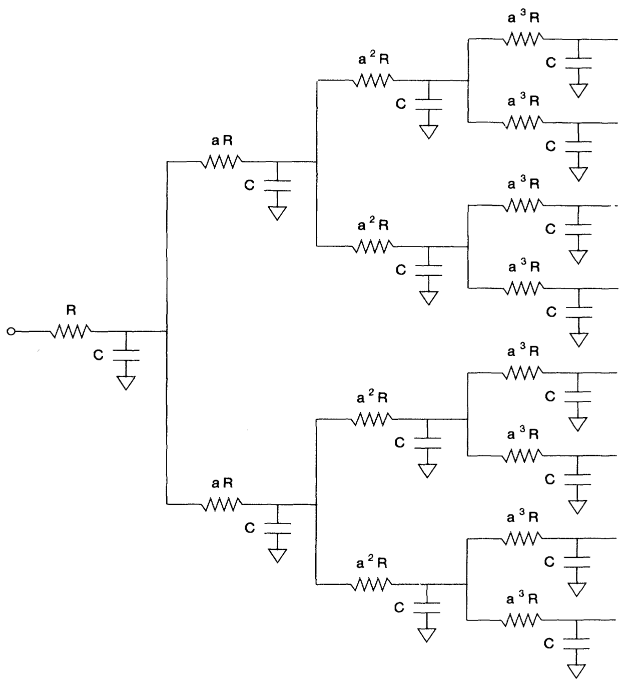

FIG. 2. Equivalent circuit for a groove of the rough-interface model in Fig. 1.

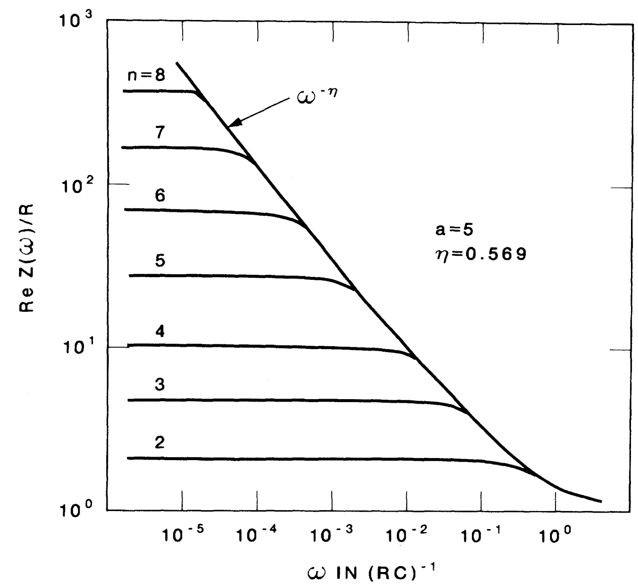

FIG. 3. Frequency dependence of the real part of the input impedance of the network in Fig. 2 for finite and infinite stages.

The impedance between the input terminal and the ground of the network in Fig. 2 has the form of a continued fraction:

$$Z(\omega)=R+\frac{1}{j\omega C+}\,\frac{2}{aR+}\,\frac{1}{j\omega C+}\,\frac{2}{a^2R+}\,\cdots, \tag{1}$$

where I have used the condensed form of writing the fraction.[7] We will study the asymptotic form of $Z(\omega)$ at low frequencies. A continued fraction of the form

$$A=b_1+\frac{a_2}{b_2+}\,\frac{a_3}{b_3+}\,\frac{a_4}{b_4+}\,\cdots \tag{2}$$

can be successively approximated by a sequence $\{A_n\}$, where A_n is the nth convergent of A, i.e., the value of the fraction which is truncated at a_n/b_n. If we write $A_n=p_n/q_n$, then p_n and q_n satisfy the recurrent relations

$$p_n=b_np_{n-1}+a_np_{n-2},\quad q_n=b_nq_{n-1}+a_nq_{n-2}. \tag{3}$$

The initial conditions are

$$p_1=b_1,\quad q_1=1,\quad p_2=b_1b_2+a_2,\quad q_2=b_2. \tag{4}$$

This method is used to evaluate the first few convergents of Z, where Z_n is the $2n$th convergent of the continued fraction in Eq. (1). It can be readily verified for $\omega RC \ll 1$ that

$$Z_1=R+1/j\omega C,\quad Z_2\cong R(1+2a/9)+1/3j\omega C,$$

etc. After a sufficient number of steps, $n\gg 1$, and for $a>2$, $\omega RC\ll 1$,

$$Z_n\cong R\frac{a(a+1)}{(a-1)(a-2)(2a-1)}\left(\frac{a}{2}\right)^n+\frac{1}{2^nj\omega C}. \tag{5}$$

One can see from Eq. (5) that

$$Z_n(\omega/a)=\tfrac{1}{2}aZ_{n-1}(\omega). \tag{6}$$

For large n, the small-ω expansion eventually breaks down, but the relation in Eq. (6) remains valid[8] and approaches the dynamical scaling law[9,10]

$$Z(\omega/a)=\tfrac{1}{2}aZ(\omega), \tag{7}$$

where $Z(\omega)=\lim_{n\to\infty}Z_n$. The solution of Eq. (7) is

$$Z(\omega)=KR(j\omega)^{-\eta}, \tag{8}$$

where K is a scale factor, and $\eta=1-\ln 2/\ln a=1-\bar{d}$. For the general model of N branches at every step, we find $\eta=1-\ln N/\ln a=1-\bar{d}$. In this way the frequency exponent of the CPA element is directly connected to the geometry of the rough interface. A smooth surface has few grooves (small N), and each branch has a large reduction ratio in area (large a). Consequently, its $\bar{d}$ is small and η is close to unity, as seen experimentally.

It is instructive to evaluate Z_n numerically for finite

n and general frequency by using the recurrent relations. The results are shown in Fig. 3, where the real part of the input impedance is plotted versus the frequency. The curve for infinite n follows the asymptotic formula for $\omega RC \ll 1$, deviates from the power law for $\omega RC \lesssim 1$, and approaches R for $\omega RC > 1$. The curves for $n \geqslant 2$ have a flat low-frequency regime with

$$\mathrm{Re}Z_n \cong R \frac{a(a+1)}{(a-1)(a-2)(2a-1)} \left(\frac{a}{2}\right)^n,$$

an intermediate-frequency regime given by the asymptotic formula, and a flat high-frequency regime. The imaginary part of the impedance, which is not plotted, has a low-frequency regime of ω^{-1}, an intermediate-frequency regime of $\omega^{-\eta}$, and a high-frequency regime of ω^{-1}. In both the real and the imaginary parts the low-frequency regime appears at lower ω for larger n. Taking these results together, one arrives at the following physical picture of the origin of the CPA element. When a signal is injected into the interface, it diffuses from one material to the other by following the RC network. The lower the frequency the more the signal travels through the resistive part of the network before being shunted across the interfacial capacitance. Since the resistance part of the network represents the irregularities of the interface, it is found that the roughness affects the low-frequency signal more than the high-frequency signal, and the effect appears as an increased impedance at low frequencies. The self-similarity property of the system gives rise to the power-law frequency dependence.

The fractal dimension of a rough surface is determined by measurement of its area using different scales. For the model interface, it is easy to find that its fractal dimension is $\bar{d}_s = 2 + \bar{d}$. Thus we can write $\eta = 3 - \bar{d}_s$. Since $\bar{d}_s$ may be measured independently, it would be interesting to see how well this relation holds for real interfaces.

The behavior of the model network is very similar to what is observed for gold films near the percolation threshold.[11] On the metal side of the threshold the low-frequency impedance levels off, while on the insulator side the resistance follows the ω^{-x} power law, where $x \cong 0.95$. The capacitance of the system has the ω^{x-1} dependence, which means that the reaction satisfies the same power law as the resistance. On the metallic side the low-frequency capacitance reaches a plateau, which corresponds to the finding that the low-frequency reactance for a finite network behaves like ω^{-1}. The gold clusters are known to be self-similar.[11] It may be possible to find a relation between the critical exponent x and the branching geometry of the percolation cluster.

The frequency response of percolation networks has been discussed on the basis of anomalous diffusion by Gefen, Aharony, and Alexander.[12] They have derived the formula $\eta = \mu/\nu(\theta+2)$ by applying the dynamical scaling argument on the conductivity. In this formula μ and ν are the critical exponents of the conductivity and the correlation length, respectively, and θ is the index for anomalous diffusion. The result for the network in Fig. 2 can be related to a modified version of their theory. It is shown in Eq. (6) that for this network the quantity which satisfies the frequency scaling relation is the impedance, or equivalently its inverse, the admittance $Y(\omega)$.[13] The latter is found by multiplication of the conductance by a length and division of the result by the cross-sectional area. For a percolation network in d dimensions, we obtain $Y(\omega) \propto \xi^{-\mu/\nu+d-2}$ in the dc limit, where ξ is the correlation length. When the dynamical scaling argument is applied to Y, we obtain $\eta = (\mu/\nu - d + 2)/(\theta+2)$. This result is equivalent to $\eta = 1 - \bar{d}/(\theta+2)$ on account of the identities $\bar{d} = d - \beta/\nu$ and $\theta = (\mu - \beta)/\nu$. One can recognize the new η as the exponent in the density of diffusion modes.[9] I will now calculate θ for the network in Fig. 2. Consider a random walk on the network. Assume that a step to the left is equally likely as a step to the right. Starting from an arbitrary junction in the middle of the network, the walker finds two paths to the right and one to the left. The average motion is steadily to the right with the distance traveled given by $n = N/3$. The quantity θ is defined by $\langle r^2 \rangle \propto N^{2/(\theta+2)}$. Hence we find $\theta = -1$. It may also be assumed that the probability of a step is proportional to the width of the path. Thus a move to the left is a times more likely than to the right. In this case $n = -(a-2)N/(a+2)$ and $\theta = -1$. Under either assumption we find $\eta = 1 - \bar{d}$. The unusual value for θ results from the topology of the network, which is that of a Cayley tree. In fact, the Cayley tree is a special case of the present network with $a = 1$, and it is physically uninteresting because its frequency exponent is $\eta = \frac{1}{2}$. It is necessary to have $a > 2$, which makes the network a fractal, to obtain nontrivial values of η.

Thermal fluctuations in a resistor produce the white spectrum of Johnson noise.[14] A generalization of the Nyquist theorem shows that the network in Fig. 2 produces a noise spectrum of $\omega^{-\eta}$.[15] This type of noise, usually called $1/f$ noise, is found in virtually all electronic components.[16] Following this investigation, I propose that the $1/f$ noise may be generated at grain boundaries of bulk metals and semiconductors, and at metal-metal, metal-semiconductor, and semiconductor-semiconductor junctions.

In summary, I propose a fractal model for the constant-phase-angle element seen at rough interfaces. The frequency dependence of the element is determined by the fractal dimension of the interface, which in turn can be measured by microscopy. The investigation may shed light on the conducting property of metal clusters near the metal-insulator transition, and the source of the $1/f$ noise in electronic components.

The author wishes to thank Dr. J. B. Bates, Dr. J. C. Wang, and Dr. T. Kaplan for informative discussions. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

[1]See the review by P. H. Bottelberghs, in *Solid Electrolytes,* edited by P. Hagenmuller and W. Van Gool (Academic, New York, 1978), Chap. 10, and references therein.

[2]R. de Levie, Electrochim. Acta **10**, 113 (1965).

[3]P. H. Bottelberghs and G. H. J. Broers, J. Electroanal. Chem. **67**, 155 (1976).

[4]R. D. Armstrong and R. A. Burnham, J. Electroanal. Chem. **72**, 257 (1976).

[5]A. Le Mehaute and G. Crepy, Solid State Ionics **9** and **10**, 17 (1983).

[6]B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).

[7]See *Handbook of Mathematical Functions,* U.S. National Bureau of Standards Applied Mathematics Series No. 55 (U.S. GPO, Washington, D.C., 1964), p. 19.

[8]T. Kaplan and L. J. Gray have derived the following exact relation:

$$Z\left(\frac{\omega}{a}\right) = R + \frac{aZ(\omega)}{j\omega CZ(\omega)+2}.$$

Equation (7) is the small-ω limit. I am grateful to Dr. Kaplan for this information.

[9]S. Alexander and R. Orbach, J. Phys. (Paris) **43**, L-625 (1982).

[10]R. Rammal and G. Toulouse, J. Phys. (Paris) **44**, L-13 (1983).

[11]R. B. Laibowitz and Y. Gefen, Phys. Rev. Lett. **53**, 380 (1984).

[12]Y. Gefen, A. Aharony, and S. Alexander, Phys. Rev. Lett. **50**, 77 (1983).

[13]The same is found for the d-dimensional Sierpinski gasket. Since at different frequencies the excitation spreads out over different volumes of the fractal, it is argued that the dynamical scaling should apply to the total admittance in the diffusion volume in general.

[14]H. Nyquist, Phys. Rev. **32**, 110 (1928).

[15]G. H. Wannier, *Statistical Physics* (Wiley, New York, 1966), Chap. 23.

[16]See the review by P. Dutta and P. M. Horn, Rev. Mod. Phys. **53**, 497 (1981), and references therein.