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IMPEDANCE OF A FRACTAL ELECTROLYTE–ELECTRODE INTERFACE

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Abstract—Recent theoretical results reported by Nyikos and Pajkossy (N-P) on fractal electrolyte/blocking electrode interfaces have been tested with numerical calculations. It is shown that (1) interfaces having electrolyte–metal boundaries in form of a generalized Koch curve do not have a constant-phase-angle impedance as they claim, (2) the fractal dimension D has little effect on the shape of the impedance *vs* frequency graphs, and (3) the relation between D and the frequency exponent n, $n = 1/(D-1)$, derived by N-P is invalid. It is demonstrated that the source of their invalid results is the use of some incorrect assumptions in their theory.

INTRODUCTION

The interfacial impedance between an electrolyte and a blocking electrode often shows a fractional-power dependence on angular frequency ω[1–2]:

$$Z(\omega) = A(j\omega)^{-n}, \qquad (1)$$

where A is independent of ω, $j = \sqrt{-1}$, and $1 > n > 0.5$. Equation (1) is a generalized form of the Warburg impedance[3] which corresponds to the case $n = 1/2$. An electrical element having an impedance in this form is sometimes called a constant-phase-angle (CPA) element[4, 5] or a non-Debye capacitor[6–8]. We shall refer to equation (1) as a CPA behavior in this paper.

Several models have been proposed to explain this behavior. According to a pore model[9] this impedance can be produced by pores with special shapes, and the value n in equation (1) is related to the detailed shape of the pore. According to Liu's fractal model[10], this impedance can be produced by some fractal interfaces specially constructed, and the frequency exponent n can be related to the fractal dimension D of the interfaces by

$$n = 3 - D. \qquad (2)$$

According to Nyikos and Pajkossy (N-P)[11], on the other hand, all fractal interfaces should have a CPA impedance, and n and D are related by

$$n = 1/(D-1). \qquad (3)$$

We have previously[12] discussed the similarities and discrepancies among these models. We demonstrated that Liu's fractal model is similar to the pore model because of the way his fractal interface is constructed, and that the validity of equation (2) depends crucially on the special way his fractal dimension is defined. We pointed out that equation (3) is questionable because our numerical results show that fractal interfaces having an electrolyte-metal boundary in the shape of a generalized Koch curve do not have a CPA impedance as N-P claimed. In this work, we present the details of these numerical results. We shall demonstrate that some assumptions used by N-P in proving the CPA nature of fractal interfaces and in deriving equation (3) are invalid.

FRACTAL MODEL OF NYIKOS AND PAJKOSSY

Two fractal interfaces used by Pajkossy and Nyikos[13] are shown in Fig. 1. Each interface consists of long parallel V-shaped grooves filled with electrolyte. The electrolyte-metal interfacial boundary forms a generalized Koch curve, the fractal dimension of which can be measured with the coastline method[14] using a pair of dividers. As indicated in the figure, this dimension depends on the angle of V-shaped grooves: the smaller the angle α, the greater the fractal dimension D.

As in Liu's fractal model[10] and in the pore model[9], the interfacial impedance in the N-P model is assumed to be produced by the resistance in the electrolyte and the double layer capacitance at the electrolyte–metal boundary. Formally, the admittance of a blocking interface can be written as[11]

$$Y = \sum_i \frac{j\omega C_i}{1 + j\omega R_i C_i}, \qquad (4)$$

where the resistance R_i and the capacitance C_i are unknown combinations of the resistance elements of the electrolyte in the grooves and the capacitance elements at the electrolyte–metal boundary. N-P claim that Y, R_i, and C_i obey the following scaling laws when the whole system is blown up spatially by a factor of r:

$$Y(r \cdot 1, \omega) = r^2 Y(1, \omega) \qquad (5)$$

$$C_i(r \cdot 1) = r^D C_i(1), \qquad (6)$$

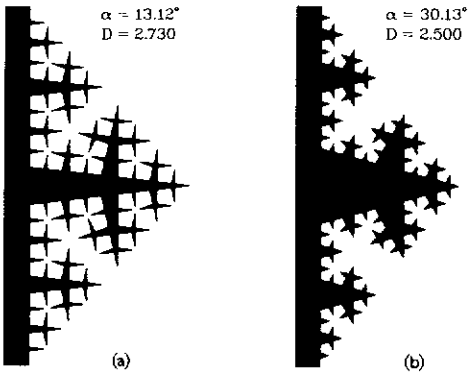

Fig. 1. Cross sections of the electrolyte–electrode interfaces considered in this work. Each electrode contains long parallel V-shaped grooves filled with electrolyte (shaded region). The angle of the grooves is denoted by α and the fractal dimension of each interface is denoted by D.

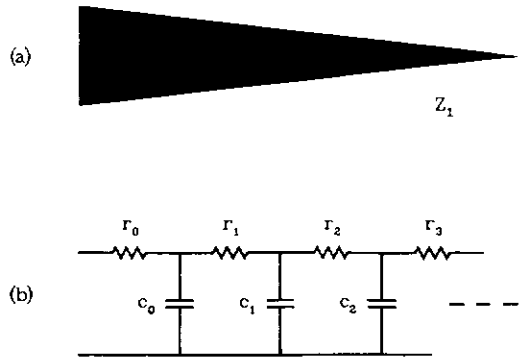

Fig. 2. (a) The structure of the smallest electrolyte-filled groove. Its impedance is represented by Z_1. (b) rc ladder network used for calculating Z_1. Each rc stage, say r_i and c_i, represents a slice of the groove.

and

$$R_i(r\cdot 1) = r^{-1}R_i(1). \tag{7}$$

In the above equations, the "1's" and the "$r\cdot 1$'s" stand for the original values and the new values after the blowup, respectively. Equations (4), (6) and (7) give

$$Y(r\cdot 1, \omega) = rY(1, \omega r^{D-1}). \tag{8}$$

From the above results, N-P reach the conclusions that for a fractal interface, Y should have a CPA behavior, and n and D should be related by equation (3). In this work, however, we show that these results are invalid. We demonstrate that equations (5) and (6) are incorrect, and equation (8) should be replaced by

$$Y(r\cdot 1, \omega) = rY(1, \omega r), \tag{9}$$

independent of the fractal dimension D.

CALCULATION METHOD

In Fig. 1a, viewing from the electrolyte side (from left to right) one finds that there is one largest groove at the middle which contains many smaller grooves of various sizes. We shall label its impedance with Z_4. There are two second largest, four third largest, and eight smallest grooves. We shall label their impedances with Z_3, Z_2 and Z_1 respectively. Besides these grooves, there are 16 flat regions on the front surface Each region has a pure capacitive impedance, which will be labeled as Z_0. The interface impedance Z is approximated by

$$1/Z = 16/Z_0 + 8/Z_1 + 4/Z_2 + 2/Z_3 + 1/Z_4. \tag{10}$$

To calculate the impedance Z_1, we follow[15–17] and divide the smallest groove into k slices at different distances from its opening. The impedance can be approximated with that of an rc ladder network as shown in Fig. 2. The resistance r_i is determined by the resistivity of the electrolyte in the groove, and the cross section and thickness of the ith slice. The corresponding capacitance c_i is determined by the double layer capacitance per unit area and the electrolyte–metal boundary area on the two edges of the slice. To calculate numerically the impedance of a ladder network, one can start from the last element from the right and use the equation[17]

$$z_{i-1} = 1/(jc_{i-1}\omega + 1/z_i) + r_{i-1}, \tag{11}$$

repeatedly from $i = k$ to $i = 1$. If the number of slices k is large enough, $z_0(\omega)$ obtained should be a good approximation to the impedance Z_1. This can be achieved by making sure that further increase of the value of k does not change $z_0(\omega)$ over the frequency range of interest.

To calculate the impedance Z_2, the branched groove (Fig. 3a) is represented by a branched rc ladder network. The impedance of each of the three branches is Z_1. These Z_1's connected in parallel to give a resultant impedance $Z_1/3$ at the intersection. Therefore, the branched ladder network can be replaced by a simple ladder network as shown schematically in Fig. 3b if $Z_1/3$ is used as the terminating impedance at the end of the network. In other words, using $z_k = Z_1/3$, equation (11) can be applied to obtain Z_2. The impedances Z_3 and Z_4 can be calculated in a similar way according to their branching configurations. Equation (10) can then be used to calculate the total impedance of the electrolyte–electrode interface. For interfaces with more stages, the labeling and calculation are similar. For example, for a five-stage interface, the impedances of the grooves are labeled by Z_0, Z_1, Z_2, Z_3, Z_4 and Z_5 and their numbers are 32, 16, 8, 4, 2 and 1, respectively.

RESULTS

In this work, all impedance calculations were made for a portion of interfaces that is 1 cm long along the direction parallel to the V-shaped grooves. The length of each segment along the Koch-curve boundaries (Fig. 1) was always taken to be 1 cm, irrespective of the number of stages used. The resistivity of the electrolyte was taken to be 10^3 ohm-cm and the double layer capacitance per unit area was taken to be 3 nF cm^{-2}. These values are supposed to be comparable to the experimental values used in[13].

The impedances calculated for the interfaces shown in Fig. 1 are shown in Fig. 4. As can be seen, the phase-

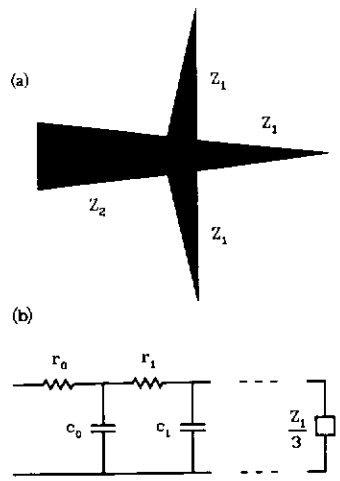

Fig. 3. (a) The structure of the second smallest groove. Its impedance is represented by Z_2. (b) *rc* ladder network used for calculating Z_2. The terminating impedance $Z_1/3$ comes from the three Z_1's connected in parallel at the intersection.

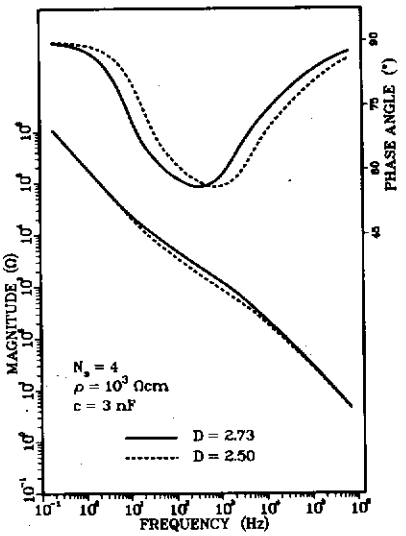

Fig. 4. Calculated impedances for the interfaces shown in Fig. 1. N_s is the number of stages of the grooves, ρ is the resistivity of the electrolyte, and c is the double layer capacitance per cm^2 of the electrolyte–metal boundary.

angle graphs are not two horizontal lines and the magnitude *vs* frequency graphs are not two straight lines, as one would expect from a CPA behavior. The graphs for the two interfaces are very similar; they are only displaced slightly from each other. These results contradict the claims of the N-P model that fractal blocking interfaces should have a CPA impedance and that the frequency exponent and the fractal dimension should be related by equation (3).

To see if the above discrepancies are due to the small number of stages used, we made a calculation for an interface having the same fractal dimension as Fig. 1a, but increased the number of stages from 4 to 10. The number of the front flat regions in this case became $2^{10} = 1024$. The width of each region was still taken to be 1 cm. The impedance and the phase-angle graphs are shown in Fig. 5. The results show that the interface does not have a CPA behavior. To understand the source of discrepancies between the results of our calculation and the N-P model, we shall now analyze the assumptions used in their theory.

Nyikos and Pajkossy claim that the scaling law of equation (5) is "well-known." However, we shall demonstrate that it is invalid. Following N-P, we assume that the impedance of an interface is formally given by equation (4). When the system is blown up spatially by a factor r, the R_i's are scaled according to equation (7), and C_i's by the equation

$$C_i(r \cdot 1) = r^2 C_i(1), \tag{12}$$

which is a special case of equation (6), $D = 2$. We use equation (12) here instead of equation (6) because we shall demonstrate that the latter is invalid and should be replaced by the former. Equations (4), (7) and (12) give

$$Y(r \cdot 1, \omega) = r^2 \sum_i \frac{j\omega C_i}{1 + j\omega R_i C_i r} \tag{13}$$

$$r^2 Y(1, \omega) = r^2 \sum_i \frac{j\omega C_i}{1 + j\omega R_i C_i}. \tag{14}$$

Comparing equations (13) and (14), one finds that equation (5) cannot be true in general for all frequencies as assumed by N-P. It is true for $\omega = 0$, and for all frequencies if R_i's vanish. In the latter case, the problem is reduced to that of a flat electrode.

Returning to equation (6), we notice that it is built upon the assumption that area changes as r^D when the system is blown up spatially by a factor r. However, geometry tells us that an area should change as r^2. For example, the 4-stage boundary surfaces shown in Fig. 1 increase by a factor r^2 when they are spatially blown up by a factor r without introducing new stages at the same time. This is the reason why equation (6) should be replaced by equation (12), *ie*, $D = 2$. One may wonder then about the meaning of the fractal dimension D. This can be illustrated by noticing that when one measures the area of the boundary surface in Fig. 1a, for example, with a pair of dividers, the result

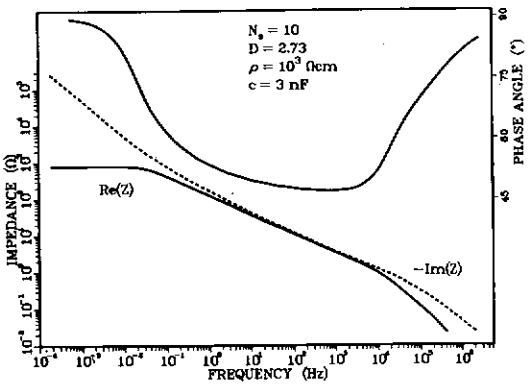

Fig. 5. Calculated impedance for an interface having the same fractal dimension as Fig. 1a, but with the number of stages increased from 4 to 10.

depends on the method used. If the structures smaller than the divider opening are neglected, as in the coastline problem[14], then the measured area depends on the measuring scale, and the fractal dimension D used by N-P can be obtained from the slope of the log (area) *vs* log (step length) graph. In other words, the scaling law suitable for blowing up a system by some factor is different from that applicable in measuring the fractal dimension of an object.

For a given real interface, when the impedance is written formally in the form of equation (4), all the detailed structures are taken into account in determining the C_i's. When blown up by a factor r, all these structures are changed by a factor r in every direction and an area should change as r^2. Therefore, equation (12), instead of equation (6), should be used.

To demonstrate numerically the above discussion about equations (5) and (6), we first calculated the admittance corresponding to the impedance of the 10-stage generalized Koch curve given in Fig. 5. Then the system was blown up spatially by a factor $r = 10$ and the new admittance was calculated. The results are shown in Fig. 6. Notice that $Y(r \cdot 1, \omega)$ cannot be obtained from $Y(1, \omega)$ by moving the latter upward by a factor $r^2 = 100$ as suggested by equation (5). On the other hand, $Y(r \cdot 1, \omega)$ can be obtained from $Y(1, \omega)$ by first moving upward by a factor $r = 10$ and then to the left by a factor r^{D-1} as suggested by equation (8), provided $D = 2$. This means that our numerical result is consistent with equations (12) and (9), but not with equations (6) and (8) used by N-P.

DISCUSSION

As shown in Figs 4 and 5, the calculated impedances for the fractal interfaces considered in this work do not have a CPA behavior as N-P have predicted from their theory. We believe the discrepancies originate from the use of invalid assumptions in their theory equations (5) and (6). We have given reasons why these assumptions are invalid and have demonstrated with numerical calculations Fig. 6 that indeed this is the case. Since the interfaces should not have a CPA behavior, the derived relation between n and D, equation (3), becomes meaningless.

Pajkossy and Nyikos[13] recently constructed electrodes with copper plates according to the patterns shown in Fig. 1 and measured the interfacial impedance using sodium sulfate solution as the electrolyte. They found very good agreement between the experiment and the prediction of equation (3). Since our calculations show that a CPA impedance cannot be obtained from the N-P model and equation (3) is meaningless, and since the use of copper plates as blocking electrodes is questionable, this agreement is an unexplained mystery.

As pointed out before[12], measuring the fractal dimension of an interface with dividers and measuring the interfacial impedance are two methods of probing the structure of the interface. In the former case, structures of sizes comparable to and larger than the divider opening are all effectively probed. However, in the impedance measurement, the current penetration depends on both the size and the location of the grooves. For example, in Fig. 1a, for some frequencies, the ionic current may reach everywhere in the smallest groove near the top of the figure, but not the smallest groove at the bottom of the largest groove. In other words, the impedance measurement does not probe the structures of the same size equally as in the fractal dimension measurement. As a consequence, there should be no simple relation between D and n even the fractal interface does have a CPA impedance. However, if the fractal dimension is defined in a way consistent with the current penetration concept as in Liu's model[10, 12], a simple relation such as equation (2) can exist. It is interesting to note that there is no universal relation in which n is simply a function of D even for Liu's model when it is generalized[18].

Bates and Chu[19] have measured the surface profiles and interfacial impedances of several electrodes. They found that the fractal dimensions of the surfaces are only slightly greater than 2 ($D = 2$ for a plane) and that there is no obvious correlation between the fractal dimension and the frequency exponent. This suggests that the CPA behavior of their electrodes may not be due to the fractal nature of the interface. It seems that at the present time, the origin of the CPA impedances observed for many interfaces is still an unsolved problem.

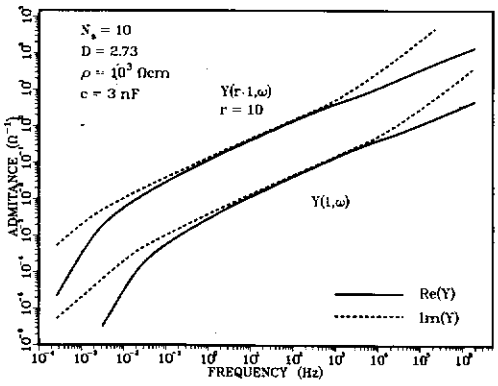

Fig. 6. $Y(1, \omega)$: Calculated admittance for an interface having the same fractal dimension as Fig. 1a, but with the number of stages increased from 4 to 10. $Y(r \cdot 1, \omega)$: The admittance of the interface when it is spatially blown up by a factor $r = 10$.

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