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LETTER TO THE EDITOR

Theory of the impedance of fractal interfaces

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Abstract. In this Letter we present a study of the frequency dependence of the impedance ($Z(\omega) \propto (\mathrm{i}\omega C)^{-\eta}$) of fractal models for the electrode–electrolyte interface. We will show that the Cantor bar model gives a fractional exponent η of this impedance for only a very limited range of parameter values while a model based on a Koch curve gives a fractional exponent over a large frequency range for a broad range of parameter values.

For the impedance of a metal electrode–electrolyte interface one finds experimentally the following dependence:

$$Z(\omega) \propto (\mathrm{i}\omega C)^{-\eta}. \tag{1}$$

This relation holds over a broad frequency range (10^{-4}–10 kHz). For more experimental details we refer the reader to Geertsma *et al* (1989). Recently the fractional exponent η of the frequency dependence of the impedance $Z(\omega)$ of a metal electrode–electrolyte interface has been the subject of a large number of theoretical studies. The purpose of this Letter is to report a study on the range of the exponent.

Le Mehaute and Crepy (1983) were the first to propose a self-similar structure of a metal electrode–electrolyte interface. However, their analysis is rather vague about the structure of such an interface. Liu (1985) realised a self-similar interface based on a Cantor bar construction (figure 1(a)). Essentially it is a self-affine structure: the geometry of each stage exactly resembles the former one when scaled horizontally by a factor a. Therefore, the resistance of the electrolyte in the bars (black area) is increased by the factor a in every stage of branching. The interfacial capacitance at the lateral sides of the bars remains the same going from one stage to another (the capacitance of the horizontal parts is not taken into account because its contribution decreases fast when going from one stage to another).

We (Geertsma *et al* 1989) based our fractal interface model on the Koch curve which represents a cross section of the interface. A straight line is divided into three equal parts and the middle one is replaced by an equilateral triangle. This procedure is repeated for each line leading eventually to a fractal structure with one scaling factor $b_0 = 3$. In figure 1(b) a cross section of the structure is given where again the black area represents the electrolyte wetting the irregular electrode surface. Going from one stage to another, only the interfacial capacitance is scaled by the geometrical scaling factor b_0.

We have shown that it is essential to take screening of grooves and bars into account. Screening of the electrical field is taken into account by means of an effective resistance

(a)

(b)

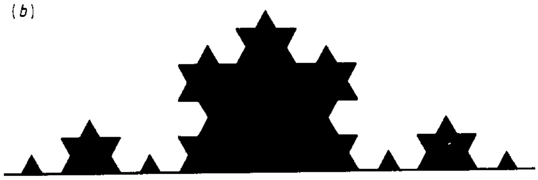

Figure 1. (*a*) Cross section of the electrode–electrolyte (black area) interface for a Cantor bar construction. (*b*) Cross section of the electrode–electrolyte (black area) interface for a Koch curve construction.

and capacitance of the grooves or bars. We have argued that these effective resistances and capacitances also scale by a constant factor going from one stage of the construction to the next. These scaling factors incorporate pure geometrical factors and a factor accounting for screening. To discuss these two interface models—the Cantor bar construction and the Koch curve construction—on an equal footing we have generalised the Cantor bar of Liu by including such screening effects. We will now discuss these two models in more detail.

If we incorporate the fact that the shape of the grooves has a large influence on the local electrical field strengths inside the grooves, we can easily generalise the Cantor bar model. The scale factor b ($\geqslant 1$) represents the scaling of the resistances due to the geometry as well as the screening of the local fields in the bars per stage, a is a similar scale factor for the capacitances and k ($\geqslant 2$) represents the branching of each groove from one stage to the next. One then finds for the impedance of the nth stage

$$Z_n(\omega) = R + 1/[\mathrm{i}\omega C + k/aZ_{n-1}(\omega a/b)]. \tag{2}$$

In figures 2(*a*) and 2(*b*) we have plotted the regions for which equation (2) shows a fractional power-law behaviour independent of the frequency as a function of a and k, respectively. In the shaded area the variation of η is at most 0.01. In the region between the hatched lines η is fractional but frequency dependent. We have checked the analytical expression as obtained by Liu (1985) for η valid in the low-frequency limit ($\omega RC \ll 1$) as a function of a

$$\eta = (\ln a - \ln k)/(\ln a - \ln b). \tag{3}$$

This equation reduces to the one derived by Liu (1985) for $b = 1$ (no screening of the bars in the vertical direction). We found that equation (3) is valid for only a very small range of parameter values of a; namely $a \leqslant 13$ and for b approaching 1; for larger values of 'a' and 'b' the fractional exponent oscillates in the low-frequency region between 0 and 2; a constant value for η as a function of frequency has not been found. From the

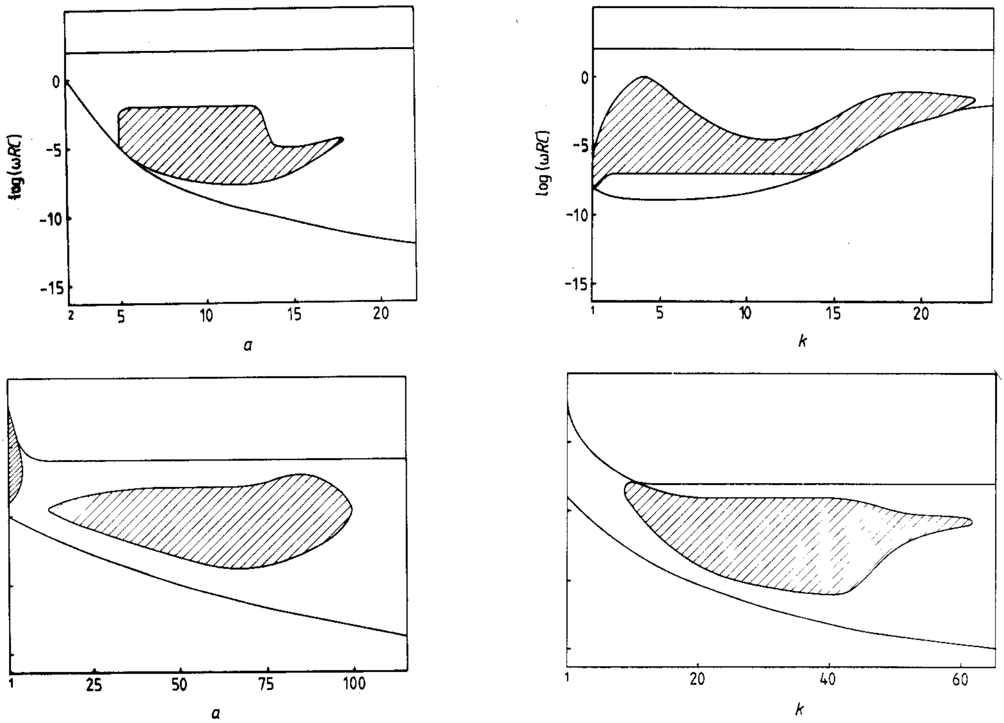

Figure 2. (a) The frequency range of the fractional exponent η calculated from (2) (Cantor bar model) as a function of the screening parameter a ($b/b_0 = 1, k = 5, n = 10$). The shaded area represents a variation in η of at most 0.01. Between the drawn lines η always lies between 0 and 1. (b) The frequency range of η calculated from (2) (Cantor bar model) as a function of the branching parameter k ($a = 10$, $b/b_0 = l$, $n = 10$). The shaded area is as defined in (a). Between the drawn lines η always lies between 0 and 1. (c) The frequency range of η calculated from (4) (Koch curve model) as a function of a ($b/b_0 = 1, k = 5, n = 10$). The shaded area is as defined in (a). Between the drawn lines η always lies between 0 and 1. (d) The frequency range of η calculated from (4) (Koch curve model) as a function of k ($a = 10, b/b_0 = 1, n = 10$). The shaded area is as defined in (a). Between the drawn lines η always lies between 0 and 1.

numerical study of this Cantor bar model it is clear that η is independent of the frequency over only a very limited frequency range for only a limited range of parameter values.

Using the parameters a and b to represent both screening and geometrical effects for the resistances and capacitances, respectively, the interfacial impedance based on the Koch curve is given as

$$Z_n^{-1}(\omega, R, C) = (k+1)/aZ_{n-1}(\omega a/b_0, R, C) + k/(R + (a/2)Z_{n-1}(\omega a/b, R, C)). \qquad (4)$$

This equation holds for a generalised Koch curve ($b_0 \geqslant 3$; $b_0 = k + 1$).

Figures 2(c) and 2(d) show the results obtained by using equation (4). We find that the region where the exponent η is frequency independent is much broader for the Koch curve model than for the Cantor bar model. So, we conclude that, in agreement with experiment, an interface construction based on the Koch curve gives a much better description for the impedance than a construction based on the Cantor bar.

From equation (4) we obtain two solutions for the fractional exponent which are valid in different parameter ranges:

$$\eta_0 = \log\{[k + 1 + 2k(b_0/b)^{\eta_0}]/a\}\log[(k + 1)/a] \qquad a \geqslant 3k + 1 \qquad (5)$$

$$\eta_1 = \log[(k + 1)/a]/\log[(3k + 1)/a] \qquad a < k + 1 \qquad (6)$$

Equations (5) and (6) give a constant η for $a \leqslant 80$. The two regions of fractional behaviour for η are separated by an area without fractional power-law behaviour: a region where η is a decreasing function of the parameters a, k ($a < k + 1$) and a region where η is an increasing function of a, k ($a \geqslant 3k + 1$). For details we refer the reader to Geertsma *et al* (1989). The same regions are found in figure 2(d).

We have shown (Geertsma *et al* 1989) that screening is essential for the fractional component to be constant over a broad frequency region for a large range of parameter values. When we ignore screening effects ($a = 1$ in the Koch model) and only vary the geometrical parameter b_0, the frequency range for which η is fractional and independent of frequency is very limited, as in the Cantor model.

We have studied the Cantor bar model for various values of the parameters a and b and compared these results with those obtained for the Koch curve model. We found that, in the case of the Koch curve model, the frequency-independent range and value of the fractional exponent are in much better agreement with experiment than is the case with the Cantor bar model.

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