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Shape-dependency of current through non-linear irregular electrodes

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Abstract

We describe a simple way to understand the non-linear response of an irregular resistive electrode in $d = 2$. It is based on the concept of an active zone in the Laplacian transfer to and across irregular interfaces. It applies to arbitrary electrode geometry and permits to compute the flux across an irregular electrode from its geometry without solving the Laplace problem. The simplifying arguments that are used are tested numerically on prefractal models of the geometrical irregularity. One finds that, for electrodes following a local Butler–Volmer response, the Tafel slope depends on the geometry. It is shown that the measure of the cell impedance leads to the determination of the actual active potential. It also gives the mean size of a part of the electrode with a surface impedance equal to the electrolyte bulk resistivity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Shape-dependency; Non-linear response; Irregular resistive electrode

1. Introduction

The effective properties of rough electrodes play an important role in the behavior of electrochemical cells [1–5]. To understand how and why geometrical irregularity influences the properties of electrodes, fractal models of electrode geometries have been introduced and studied. At first, the goal was to explain the very frequent constant phase angle behavior found in impedance spectroscopy. Even if it is now known that this explanation is not general [6,7], this approach has been fruitful because the understanding of fractal interfaces has proven to give very simple tools to understand impedance spectroscopy of irregular interfaces whatever their geometry. This is a situation where the electrode works in the linear regime when the local current density flowing across the interface is proportional to the local potential drop across the interface [8–10]. However, in most practical uses, real electrodes work under a non-linear current/potential relation as soon as the local potential drop at the interface is larger than tens of millivolts.

The purpose of this work is to extend and verify numerically the concepts used for the linear regime, namely the land surveyor method, to the non-linear transfer across irregular interfaces. Here again, we will use fractal models for the geometry, working under the implicit assumption that if one understands the basic physical features governing the behavior of non-linear fractal electrodes, one has tools to understand the behavior of any irregular non-linear system. The interest of using fractal models lies in the possibility to write analytical solution for the quantities which govern these phenomena. The analytical results are then tested by comparison with direct finite elements computations. These comparisons validate the approximations used in the theory.

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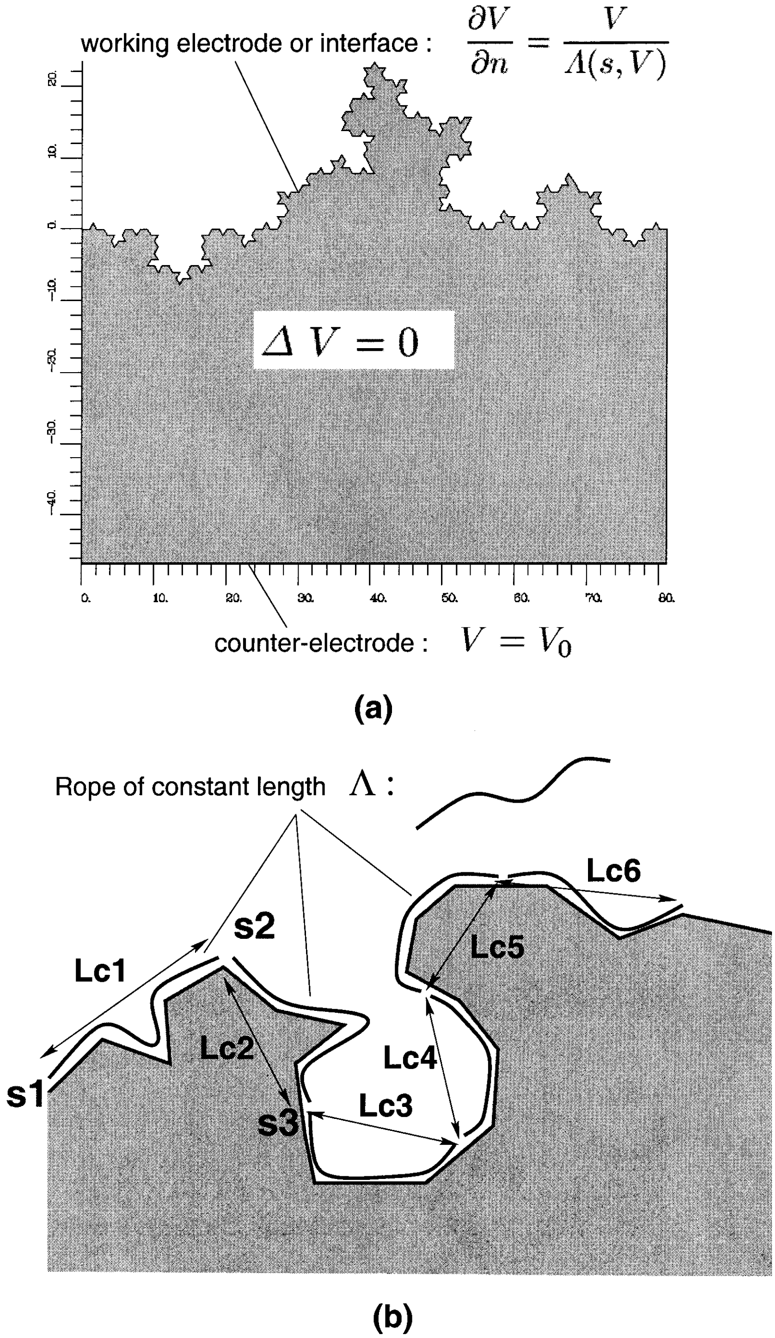

Fig. 1. (a) The irregular electrode of interest (the working electrode in electrochemistry) has an inner cut-off l and a size or diameter L. In the particular case represented here, the fractal dimension is $D_f = \log 4/\log 3$. This paper deals with the electrochemical problem where the applied voltage on the cell is V_0 on the planar counter electrode and 0 on the working electrode. (b) Land surveyor method: the curvilinear distance between the ends of a grain is equal to Λ. In the non-linear case that we consider, the rope length Λ depends on the local potential. It is smaller in the active zone of the electrode.

2. Linear reformulation of the non-linear problem

2.1. Description of the problem

We consider a two-dimensional domain Ω of conductivity σ, limited by an upper rough or irregular electrode $\partial\Omega_1$, and a flat counter-electrode $\partial\Omega_2$ (Fig. 1a). The electric current density is given by $\vec{J} = -\sigma\,\overrightarrow{\mathrm{grad}}\,V$ and the electrostatic field V in the domain Ω obeys then to a Laplace equation:

$$\Delta V = 0 \qquad (1)$$

$\partial\Omega_1$ is a flat metallic electrode on which a constant bias V_0 is applied. $\partial\Omega_2$ is a rough grounded electrode of resistivity r. In general the local d.c. current density across an electrode obeys the Butler–Volmer equation

$$j = j_0\{\exp[(1-\beta)ZeV/kT] - \exp[-\beta ZeV/kT]\} \qquad (2)$$

where Ze is the ionic charge, k is the Boltzmann constant, T the temperature and β is a number smaller than 1, called the cathodic transfer coefficient [11]. Note that for the linear regime ($ZeV/kT \ll 1$) we have $j = j_0 ZeV/kT$ and consequently the Faradaïc surface resistance is related to j_0 by $r_0 = V_j = kT/Zej_0$. If we work with positive voltage, the Butler–Volmer equation simplifies to $j = j_0 \cdot \{\exp[(1-\beta)ZeV/kT] - 1\}$. This means that there exist locally on the electrode a non-linear surface resistivity $r(V)$ which is given by

$$r(V) = \frac{V}{j_0\left(e^{\frac{(1-\beta)ZeV}{kT}} - 1\right)} \qquad (3)$$

This resistivity depends on the local potential drop. Calling s the curvilinear abscissa on the working electrode, this can be written as a non-linear boundary condition $r(s, V(s))J(s) = V(s)$ between the local current density and the value of the electrostatic potential at the rough interface. The conservation of charge implies that

$$\vec{J}\cdot\vec{n} = \sigma\frac{\partial V}{\partial n} = \frac{V}{r(s, V)} \qquad (4)$$

This non-linear boundary condition makes this problem very difficult to solve in general, especially for irregular electrodes. The following discussion presents an approximate way to deal with this question. It is based on the so-called land surveyor method that was introduced to solve this problem for the linear case [10,12].

2.2. The land surveyor method in the linear case

Let us consider the most simple description of an irregular physical surface which is the ratio of the perimeter L_p divided by its size L. Following Refs. [13,14], we call this number S:

$$S = \frac{L_\mathrm{p}}{L} \qquad (5)$$

This number S, which geometrical signification is apparently trivial, has in fact a very important meaning in characterizing the screening of the irregular structure for ordinary Laplacian fields. One knows from Makarov's theorem [15] that, with the Dirichlet boundary condition ($V = 0$), the active zone, that is the zone where the current accumulates, has a size $L \simeq L_{\mathrm{act.}}$ whatever the geometry. Then trivially,

$$L_{\mathrm{act.}} \simeq \frac{L_\mathrm{p}}{S} \qquad (6)$$

and consequently $1/S$ can be considered as the 'screening efficiency' due to the irregularity of the geometry, for the Dirichlet boundary condition.

It is shown in [12] that a coarse-graining technique allows to transform the mixed boundary condition into a purely Dirichlet condition ($V = 0$) but on a new geometry. This new geometry is made of macrosites of perimeter $\Lambda = \sigma r$. Because in the new coarse-grained geometry, we are dealing with a purely Laplacian field, we can use the screening factor $1/S_{\mathrm{cg}}$ of this object to find the effective impedance

$$Z(r) = Z_\mathrm{p}(r)S_{\mathrm{cg}} \qquad (7)$$

where $Z_\mathrm{p}(r)$ would be the surface impedance of a 'stretched' electrode with a length L_p. In this frame, the number S_{cg} of the coarse-grained object determines directly how the impedance of the total surface is multiplied due to screening.

This method applies to any irregular geometry provided that we have an image of the electrode. All what we need is a rope of length $\Lambda = \sigma r$ [16] (Fig. 1b). If N_p is the total number of grains of perimeter Λ with diameters $L_1, L_2, \ldots, L_{N_\mathrm{p}}$, one has $Z_\mathrm{p}(r) = r/b\Lambda N_\mathrm{p} = 1/\sigma N_\mathrm{p} b$, where b is simply the thickness of the cell in the third dimension. The screening factor of the coarse-grained electrode is equal to $N_\mathrm{p}\langle L_\mathrm{g}\rangle L$, so that the electrode impedance is finally

$$|Z| = \frac{1}{\sigma b}\frac{\langle L_\mathrm{g}\rangle}{L} \qquad (8)$$

where $\langle L_\mathrm{g}\rangle$ is the average of the grain diameter over the coarse-grained electrode. This expression applies to the case where the Faradaïc resistance is constant over the electrode.

This result has been extended to the case where the Faradaïc resistance varies along the electrode [9]. In that case, the previous result has to be written

$$|Z| = \frac{1}{\sigma b}\frac{\langle L_\mathrm{g}\rangle_{\mathrm{H}}^{\mathrm{act.}}}{L} \qquad (9)$$

where $\langle L_\mathrm{g}\rangle_{\mathrm{H}}^{\mathrm{act.}}$ represents the harmonic mean of the grain diameter taken over the active zone of the electrode.

This is the result which can be transposed to the non-linear case.

2.3. The non-linear case

If we call V^* the potential satisfying the non-linear system of Eqs. (1) and (4), we can define a fixed resistivity distribution $r^*(s)$ as the resistivity distribution on the rough electrode $\partial\Omega_1$ calculated with potential V^*:

$$r^*(s) = r(s, V^*(s)) \tag{10}$$

It is then straightforward that V^* is also solution of the following linear problem:

$$\Delta V = 0 \text{ in } \Omega$$

$$V = V_0 \text{ on } \partial\Omega_2$$

$$\frac{\partial V}{\partial n} = \frac{V}{r^*(s)} \text{ on } \partial\Omega_1 \tag{11}$$

In other words, the solution V^* of the non-linear problem is also solution of a linear problem with an inhomogeneous resistivity distribution $r^*(s)$. One is back in the situation of the preceding case of a distributed Faradaïc resistance. The land surveyor method can then be used to link the electrode impedance to this distributed resistivity $r^*(s)$.

Because $r^*(s)$ depends on the potential through the non-linear boundary condition, so will the electrode impedance. As the real potential seen by the electrode depends on this impedance, a self-consistent equation for the potential can be written.

2.4. Self-consistent approach

2.4.1. Potential of the active zone

It has been seen in Section 2.2 that, in the linear case, the working electrode can be schematically separated into two regions: a first region where most of the total current crosses the electrode, called the active zone, and a second region which is totally passive in first approximation.

In the non-linear case, the largest current densities correspond to the largest values of the local potential. These potential values are also those for which the local resistivity r varies very rapidly (exponentially) with the local potential. In other words, a small change in the local potential would induce a dramatic change in the current crossing the interface. Because the active zone is defined as the part of the coarse-grained electrode where the grains receive the major part of the current, the potential on the active zone has to be quasi-uniform. This potential is called $V_{\text{act.}}$ in the following,

2.4.2. Dividing the cell into two subsystems

From the observation of the topography of the iso-curves of the potential shown in Fig. 2a, one can see that the electrochemical cell can be divided into two subsystems as indicated in Fig. 2b. The first subsystem corresponds to the access bulk between the flat counter-electrode and an almost flat iso-curve of the potential taken very near the rough electrode. This subsystem has an impedance Z_{bulk}. One can define an equivalent height of the cell as $h = (b\sigma L Z_{\text{bulk}})$. This parameter, homogeneous to a length, can be understood as the height of the domain of width L that would have the same impedance as the first susbsystem. It is very close to the actual height of the cell and can be accessed through impedance spectroscopy at high frequency.

The second subsystem is comprised of the rough electrode plus the small volume between it and the flat iso-curve of potential. The distance between this iso-curve and the electrode is typically of the order of magnitude of the macroscopic roughness of the electrode. Its impedance is dominated by the electrode impedance [10]. Therefore, the potential on the nearby iso-curve is very close to the active potential $V_{\text{act.}}$. This subsystem has an impedance Z_{ode}.

The current flowing through the system can be expressed in two ways. First, it is the response of the whole system, including the rough resistive electrode $\partial\Omega_1$ to an applied bias V_0. The total current flowing through the cell can then be expressed as:

$$I_{\text{tot}} = \frac{V_0}{Z_{\text{bulk}} + Z_{\text{ode}}} \tag{12}$$

According to Eq. (9), the electrode impedance is:

$$\begin{aligned} Z_{\text{ode}} &= (b\sigma)^{-1} \frac{\langle L_g(r(s, V_{\text{act.}}))\rangle_{\text{H}}^{\text{act.}}}{L} \\ &= Z_{\text{bulk}} \frac{\langle L_g(r(s, V_{\text{act.}}))\rangle_{\text{H}}^{\text{act.}}}{h} \end{aligned} \tag{13}$$

Secondly, it is also the current flowing through the first subsystem with an applied bias equal to $(V_0 - V_{\text{act.}})$:

$$I_{\text{tot}} = \frac{V_0 - V_{\text{act.}}}{Z_{\text{bulk}}} \tag{14}$$

One can then see that the experimental measurements of V_0 and I_{tot}, together with the knowledge of L and h, give access independently to $V_{\text{act.}} = V_0 - (h/\sigma b L) I_{\text{tot}}$ and to $\langle L_g\rangle_{\text{H}}^{\text{act.}}(\sigma b L) Z_{\text{ode}} = (\sigma b L) I_{\text{tot}}/\text{V}_{\text{act.}}$.

2.4.3. Self-consistent formulation

From Eqs. (12)–(14), one can deduce a relation linking the value $V_{\text{act.}}$ of the potential in the active region of the electrode with the harmonic mean of the chord length in the same region:

$$\left(\frac{V_0}{V_{\text{act.}}} - 1\right)^{-1} = \frac{\langle L_g(r(s, V_{\text{act.}}))\rangle H^{\text{act.}}}{h} \tag{15}$$

This equation, although approximate, can be applied whatever the geometry. In order to use it practically, it

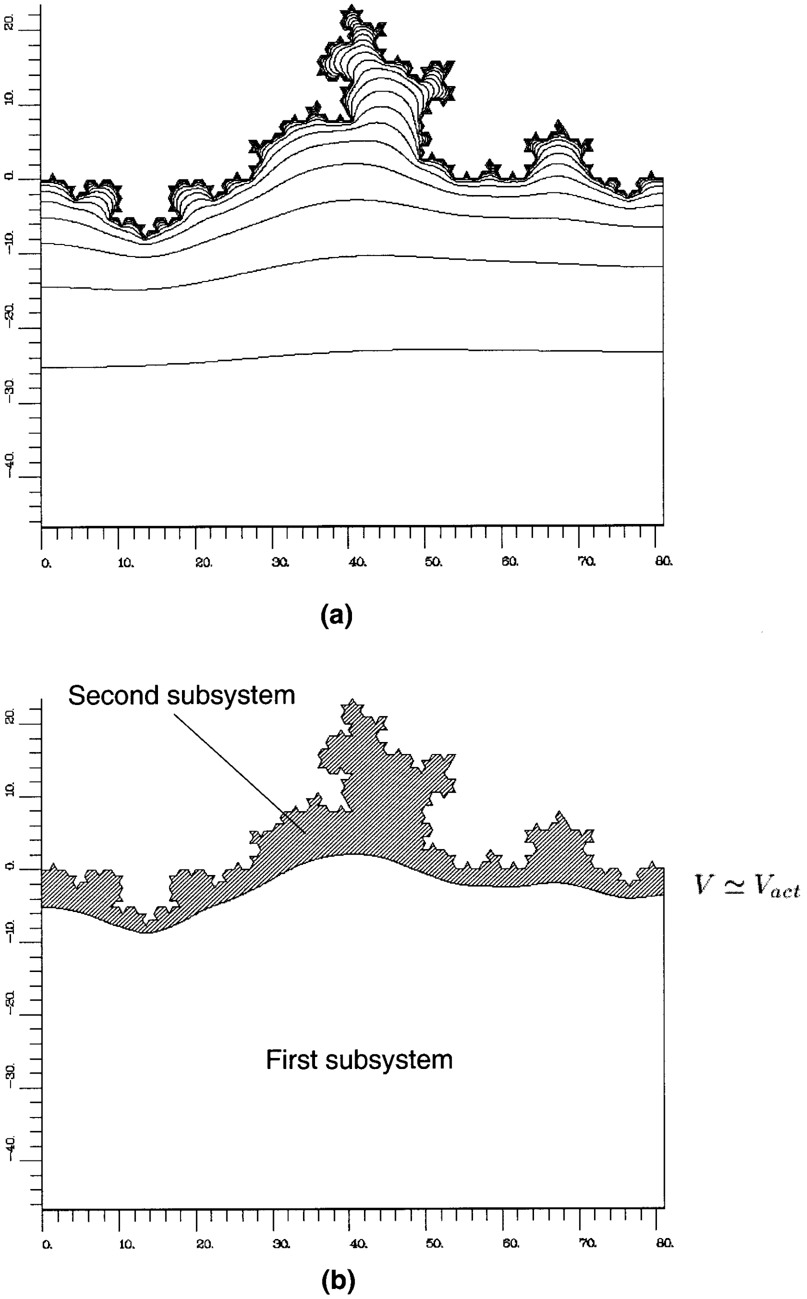

Fig. 2. Distribution of the electrostatic potential in the electrochemical cell: (a) iso-curves of the potential. One can see that an almost flat iso-curve (of potential $V \simeq V_{\mathrm{act.}}$) can be found very near the working electrode. (b) schematic division of the system into two subsystems.

is necessary to first compute the d.c. non-linear response from which the distribution of the active resistance can be found and then iterate this process through this self-consistent equation. In the particular case of a homogeneous roughness, like that of a self-similar electrode, the equation simplifies to a directly soluble problem.

2.4.4. Homogeneous roughness

We already saw that the impedance electrode has a very simple expression that uses the harmonic mean of the size grain along the rough electrode. Because the potential on the active zone $V_{\mathrm{act.}}$ is constant and the geometry the same everywhere, the local resistivity is then $r_{\mathrm{act.}} = r(V_{\mathrm{act.}})$ and the parameter Λ:

$$\Lambda(V_{\mathrm{act.}}) = \sigma r(V_{\mathrm{act.}}) \tag{16}$$

The electrode impedance now depends only on the value of the potential in the active region, and Eq. (15) can be written in the form of a self-consistent equation:

$$\left(\frac{V_0}{V_{\mathrm{act.}}} - 1\right)^{-1} = \frac{L_g(\Lambda(V_{\mathrm{act.}}))}{h} \tag{17}$$

Now $V_{\mathrm{act.}}$ is the only unknown variable. This self-consistent equation can also be rewritten as:

$$V_{\mathrm{act.}}\left(1 + \frac{h}{L_g(\sigma r(V_{\mathrm{act.}}))}\right)^{-1} = V_0 \tag{18}$$

3. Application to the non-linear response of a fractal electrode

3.1. Analytical expression of the response

In that case, the roughness of the electrode can be modelized by a fractal geometry with dimension D_f. In this modelization, the geometry is characterized by a smaller cut-off l, which represents the scale of the smallest features of the electrode, and an upper cut-off L which is the typical size (or diameter) of the macroscopic system. Calling L_p the perimeter of the rough electrode, the value of the grain size follows then a monotonic dependency on the parameter Λ:

$$\begin{aligned} L_g &= \Lambda \quad \text{if } \Lambda < 1 \\ L_g &= l\left(\frac{\Lambda}{l}\right)^{\frac{1}{D_f}} \quad \text{if } l < \Lambda < L_p \\ L_g &= \frac{L}{L_p}\Lambda \quad \text{if } \Lambda > L_p \end{aligned} \tag{19}$$

Hence, the potential $V_{\mathrm{act.}}$ on the active region on this prefractal electrode satisfies one of the following equations:

$$\begin{aligned} &V_{\mathrm{act.}} + h\frac{V_{\mathrm{act.}}}{\Lambda(V_{\mathrm{act.}})} = V_0 \quad \text{if } \Lambda(V_{\mathrm{act.}}) < 1 \\ &V_{\mathrm{act.}} + \frac{h}{l^{1-\frac{1}{D_f}}} V_{\mathrm{act.}}\Lambda(V_{\mathrm{act.}})^{-\frac{1}{D_f}} = V_0 \quad \text{if } l < \Lambda(V_{\mathrm{act.}}) < L_p \\ &V_{\mathrm{act.}} + h\frac{L_p}{L}\frac{V_{\mathrm{act.}}}{\Lambda(V_{\mathrm{act.}})} = V_0 \quad \text{if } \Lambda(V_{\mathrm{act.}}) > L_p \end{aligned} \tag{20}$$

The value of the electrode impedance is thus obtained by replacing the solution $V_{\mathrm{act.}}$ of these equations into Eq. (15). For example, in the fractal intermediate regime, the potential $V_{\mathrm{act.}}$ is solution of:

$$V_{\mathrm{act.}} + B\frac{\left(\exp\left(\frac{(1-\beta)ZeV_{\mathrm{act.}}}{kT}\right) - 1\right)^{\frac{1}{D_f}}}{\left(\frac{(1-\beta)ZeV_{\mathrm{act.}}}{kT}\right)^{\frac{1}{D_f}-1}} = V_0 \tag{21}$$

with

$$B = \frac{kT}{(1-\beta)Ze}\frac{h}{l}\left(\frac{l}{\sigma r_0}\right)^{\frac{1}{D_f}}$$

The solution $V_{\mathrm{act.}}$ of this equation, that can be solved in general only numerically, is then injected into the equation

$$Z_{\mathrm{ode}}^{\mathrm{theor.}} = (b\sigma)^{-1}\frac{L_g\left(\frac{\sigma V_{\mathrm{act.}}}{j_0\left\{e^{\frac{(1-\beta)ZeV_{\mathrm{act.}}}{kT}} - 1\right\}}\right)}{L} \tag{22}$$

This value will be compared later with values of the electrode impedance directly obtained from finite elements numerical simulation of the non-linear 2D problem.

3.2. Tafel behavior on a fractal electrode

One can also compute from Eq. (21) the current I_{tot} flowing through the electrode in the fractal intermediate regime:

$$\begin{aligned} I_{\mathrm{tot}} &= \frac{V_0 - V_{\mathrm{act.}}}{Z_{\mathrm{bulk}}} \\ &= \frac{kT}{(1-\beta)Ze}\frac{L}{l}b\sigma\left(\frac{l}{\sigma r_0}\right)^{\frac{1}{D_f}}\frac{\left(e^{\frac{(1-\beta)ZeV_{\mathrm{act.}}}{kT}} - 1\right)^{\frac{1}{D_f}}}{\left(\frac{(1-\beta)ZeV_{\mathrm{act.}}}{kT}\right)^{\frac{1}{D_f}-1}} \end{aligned} \tag{23}$$

When the applied potential on the rough electrode is much larger than kT/Ze, one finds back a Tafel's law [11]:

$$I_{\mathrm{tot}} = (j_0 L b)\left(\frac{\sigma V_{\mathrm{act.}}}{l j_0}\right)^{1-\frac{1}{D_f}}\exp\left(\frac{1-\beta}{D_f}\frac{ZeV_{\mathrm{act.}}}{kT}\right) \tag{24}$$

For $D_f = 1$, one recovers the usual law for planar electrodes under the same condition $ZeV/kT \gg 1$. For fractal electrodes, there exists a strong modification of the response due to the fractal geometry because the fractal dimension enters the argument of the exponential. One usually study in electrochemistry the so-called Tafel plots which are plots of log(I) as a function of V [11]. For an ordinary case ($D_f = 1$) one finds a straight line and the slope of this line gives a measure of the quantity $(1-\beta)$. Here, apart from the slight discrepancy due to the $V^{(D_f-1)/D_f}$ factor, one will also find a straight line but now the slope will involve $(1-\beta)/D_f$ instead of $(1-\beta)$. The effective Tafel slope is then divided by the fractal dimension [17]. This fact has already been indicated by Nyikos and Pajkossy [18] for specific self-affine model electrodes for which specific computations can be made and discussed for self-similar electrodes by Mulder et al. [19]. What we add here is a very simple geometrical interpretation which relates the size of the coarse-graining to the applied potential and permits to find directly the size of the active zone.

3.3. Numerical simulations

In order to test the validity of the coupled Eqs. (21) and (22), numerical simulations were carried out. The 2D non-linear PDE problem was solved by means of finite elements using a P1-interpolation of the electric potential, an automatic triangular meshing through Delaunay–Voronoï tesselation [20] and a Newton–Raphson resolution scheme. The geometry of the electrode is a random quadratic Koch curve (Fig. 1a) of dimension $D_f = \log(4)/\log(3)$.

We have studied the current and potential distributions along the electrode for several applied bias V_0. The results are shown in Fig. 3. One observes that the value of the peak potential in the active zone is approximately constant. On the other hand, for large applied bias, the small variations of the local potential induce much stronger variations of the current distribution. Note that the strong non-linearity of the resistivity of the electrode creates a very high spatial selectivity of the active zone.

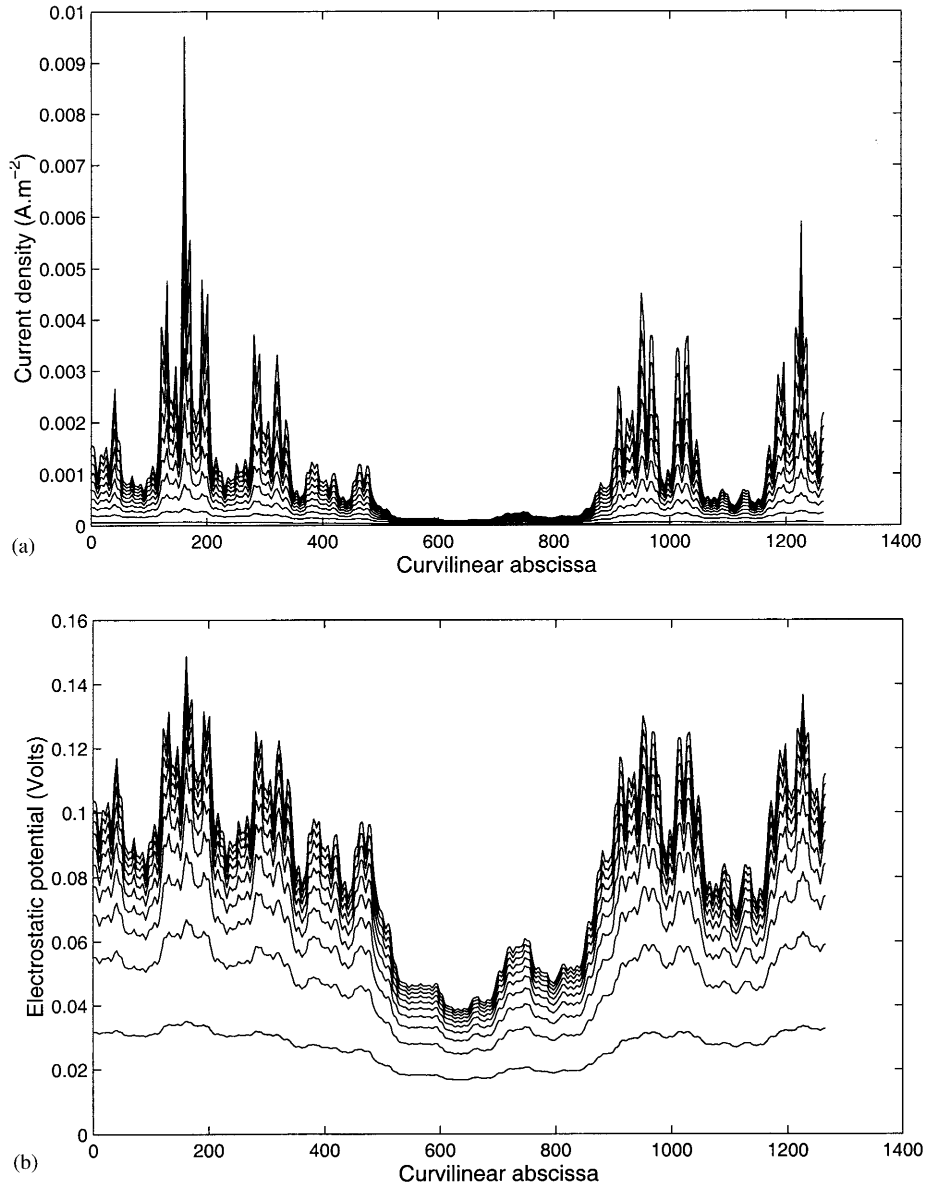

Fig. 3. Current and potential distribution. Top: current distribution along the electrode in Fig. 1 for applied bias ranging from 5 mV up to 1 V by steps of 100 mV. Bottom: corresponding potential distribution.

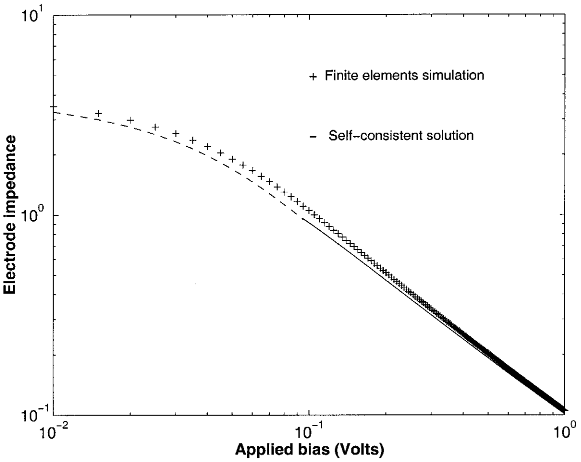

Fig. 4. Impedance curve for a Butler–Volmer response of the electrode surface. Comparison between finite element numerical simulations and solution of the self-consistent equation based on the land surveyor method. The numerical simulations were carried out with the following parameter values: $b = 1$, $\sigma = 1$, $\beta = 0$, $r_0 = 1000$, $kT/Ze = 0.025$. Impedances are measured in units of $(\sigma b)^{-1}$. The dashed line corresponds to the resolution of the self-consistent equation in the low voltage regime where Λ is larger than the perimeter of the electrode L_p The continuous line corresponds to the intermediate fractal regime.

Fig. 4 presents the electrode impedances obtained first by finite elements numerical computation of the current distribution, and second by use of Eqs. (21) and (22). One finds a good agreement, which validates the use of the land surveyor method approximation.

4. Conclusion

In summary, we have briefly recalled the concept of active zone in electrodics. This idea consists in splitting the current distribution on an irregular electrode in two zones, one uniformly active, and the second totally passive. This concept permits to model simply the behavior of a non-linear electrochemical cell through an approximation called the land surveyor method first introduced to explain impedance spectroscopy of irregular electrodes. This leads to a simple and general method to find the response of irregular electrodes in the non-linear response regime from their images only. This method yields to a simple self-consistent formulation of the problem.

It has been shown that a simple measurement of the global impedance of a cell in the non-linear regime permits the determination of the active potential and of the average size of an active grain that works uniformly. It is striking that such a complex behavior (as displayed in Fig. 3) is finally described by a simple equation.

In the particular case of a known prefractal geometry, this equation can be explicitly solved. It predicts that the slope of the Tafel plot depends on the electrode geometry. The quality of the approximations has been verified numerically through a comparison with a finite element computation of the non-linear response. One should note that the physical model can be applied as such as long as diffusion currents can be neglected, especially in solid electrolytes.

The same method should also apply to irregular electrodes in $d = 3$. In the same spirit, it could be used in the study of active transfer across irregular membranes, in heterogeneous catalysis on porous catalysts [8]. It also could play a role in the properties of semiconductor p–n junctions with irregular geometries.

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