

A Simple Method to Compute the Response of Non-Homogeneous and Irregular Interfaces: Electrodes and Membranes

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Abstract. — We present a detailed numerical test of the coarse-graining method proposed by Sapoval to compute the flux through an irregular interface in the case where the local response is inhomogeneously distributed. It is shown, through comparison with detailed finite elements simulations, that this method permits to deduce the flux across an irregular interface from its topography only, as for example in the case of non-uniform polarizability in electrochemistry. The interest of the method lies in its computational simplicity. It then constitutes an essential step towards the understanding of the flux across irregular interfaces in non-linear regimes.

Introduction

We consider here the linear transport across irregular interfaces, a common phenomenon in many natural or industrial processes. One example is the electrical response of electrodes in contact with electrolytes. Another example is the transport to and across a membrane where neutral reacting species are brought to the surface by diffusion currents instead of electrical currents in electrochemical systems. The same problem arises in the Eley-Rideal mechanism in heterogeneous catalysis where reactants have to diffuse to a catalytic porous surface in order to react. Its frequent occurrence and its practical importance has justified numerous studies of the influence of the interface geometry on the net flux across such interfaces [1].

Fractal geometry has been extensively used as a model for extreme geometrical irregularity for several reasons. It first provided some hope to better understand the ubiquitous constant phase angle response in electrochemistry [1, 2]. The possible role of the fractal structure of the interface has been extensively studied and several results have been obtained, especially in 2-dimensional systems. For a review of the early works on fractal electrodes see [1, 2] and the references therein. Secondly one can hope that understanding the behavior of fractal electrode would lead to the understanding of the role of geometrical irregularity in general even when it is not fractal. This second goal has been partly realized for the linear response of 2D-electrodes of arbitrary geometry [3, 4].

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The purpose of this paper is first to extend the finite scale renormalization procedure, proposed in [3], to the case of an irregular (self-similar) electrode with a non homogeneous distribution of the local transport parameter. This finite size real space renormalization procedure was called the “rope walk” in reference [5]. It is called here “the land surveyor” method because it is based on geometrical measurements made on the topography of the electrode.

Our second motive is to explore the use of finite elements method to compute numerical solutions of the Laplacian field with mixed boundary conditions. This type of method is required in order to study the non-linear response of irregular interfaces.

We study here situations where both the geometry and the local transport properties are irregular. We first recall briefly the nature of the problem that we address. Consider the electrochemical cell shown in Figure 1a. The response of this cell is governed by the resistivity ρ of the electrolyte and by the rate of charge transfer occurring at the interface. We restrict our study to the case where the smallest geometrical feature ℓ of the geometry is much larger than the Debye length. Consequently we may use the Laplace equation $\Delta \mathbf{V} = 0$ instead of the Poisson equation for the electrical potential in the bulk of the electrolyte. The transport equation in the volume is $\mathbf{J} = -\nabla \mathbf{V} / \rho$ where \mathbf{J} is the vector current in the electrolyte.

The rate of charge transfer at the interface is characterized by a resistance per unit surface r (known as the Faradaic resistance) and, if any, by a capacitance γ per unit surface but we restrict here to the study of the Faradaic d.c.-response. Hence the current at the surface is $\mathbf{J}_n = -\mathbf{V} / r$ where \mathbf{V} is the local potential in the electrolyte at some point “very near” the interface. Here the Faradaic resistance r has a space dependence $r(s)$ as a function of the curvilinear abscissa s as indicated in Figure 1a. We then consider the DC-problem as illustrated in Figure 1a where the outer electrode is at potential \mathbf{V}_0 and the inner electrode at zero potential. Due to charge conservation, the current $\mathbf{j}_n(s) = -\mathbf{V} / r(s)$ crossing the electrode surface must be equal to the Ohmic current $\mathbf{j}_n = -\nabla_n \mathbf{V} / \rho$ reaching it from the bulk. As a consequence the d.c. boundary condition can be written as

$$\mathbf{V} / \nabla_n \mathbf{V} = r(s) / \rho = \Lambda(s). \quad (1)$$

This introduces a local physical length scale $\Lambda(s)$ in our problem. From a mathematical point of view, the problem is to find the properties of the Laplacian field on the surface with the so-called Fourier or mixed boundary condition (1). The role of the length Λ on the current distribution on irregular electrodes was already recognized in the late forties in the case of the homogeneous response (with uniform r) [6, 7].

The equivalent circuit of a cell like that of Figure 1a is made of two resistances in series: the resistance of the electrolyte R_0 which is proportional to the electrolyte resistivity ρ and depends on the geometry of the cell, and the resistance of the electrode Z_{ode} which depends on r and on the geometry such that

$$Z_{cell} = R_0 + Z_{ode}. \quad (2)$$

Our aim here is to compute and discuss the electrode impedance Z_{ode} .

The “Land Surveyor” Method

This method permits in principle to compute Z_{ode} from the topography of the electrode and the function $\Lambda(s)$ only. It was proposed in reference [3]. We extend it to non-homogeneous surfaces. The idea is to substitute the problem of Laplacian transfer across the real electrode (which presents a finite transfer rate) by a problem of Laplacian field obeying the Dirichlet

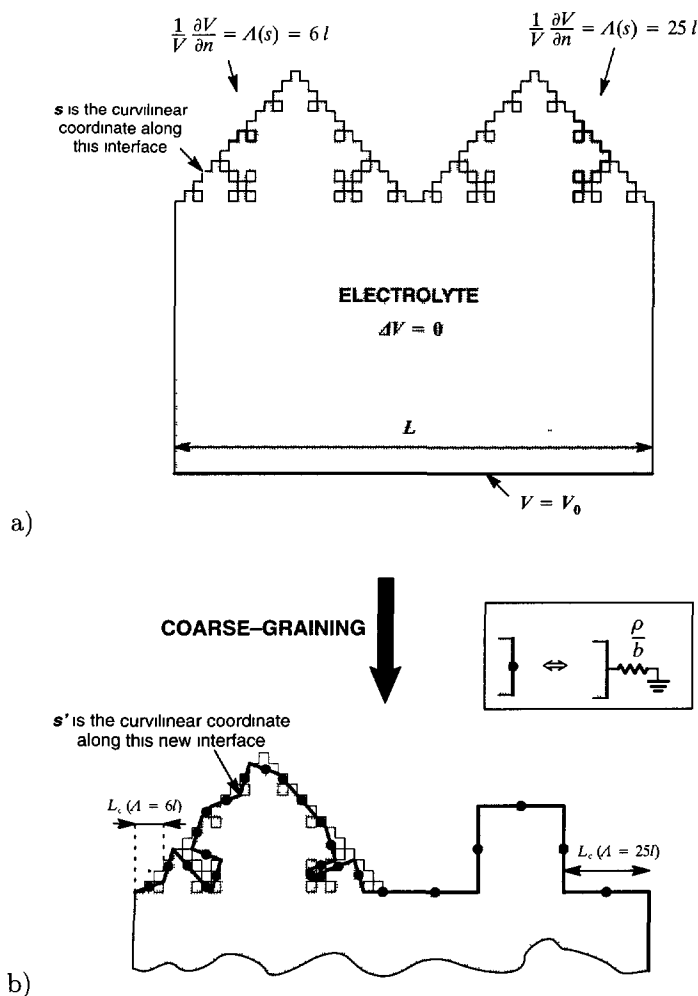


Fig. 1. — Top: schematic representation of the type of electrochemical cell under study. The electrode has an irregular geometry schematized here by a self-similar fractal and also an inhomogeneous resistivity r . In the example shown here the left part presents $r = 6\rho\ell$ while the right part presents $r = 25\rho\ell$. The curvilinear coordinate along the electrode geometry is s . Bottom: result of the coarse-graining procedure on the upper electrode. The curvilinear coordinate along this new geometry is s' and the perimeter of this new curve is $L_{p'}$. This figure is given here as an example: the computations have been carried on half of this cell.

boundary condition ($\mathbf{V} = 0$) but with a different geometry, obtained by a coarse-graining of the real geometry to a physical scale determined by the length $\Lambda(s)$.

The Dirichlet Laplace problem ($\mathbf{V} = 0$) on irregular electrodes has been thoroughly studied, at least in $d = 2$. Note that the Dirichlet problem is known as that of “primary current distribution” in the field of electrochemistry. More specifically an important theorem, Makarov’s theorem, describing the properties of the current distribution on an irregular (possibly fractal) electrode can be used [8, 9]. *This theorem states that the information dimension of the harmonic measure (here the harmonic measure is the normalized current density) on a singly*

connected electrode in $d = 2$ is exactly equal to 1. This very special property of the Laplacian field can be illustrated in the following manner: whatever the shape of the working electrode, the size of the region where most of the current flows is proportional to the overall size (or diameter) L of the electrode under a dilation transformation.

This result has a simple but profound meaning in terms of the screening efficiency of the geometrical irregularity, and this is what we use here. We consider the simplest description of an irregular electrode: the ratio $S = L_p/L$ of the perimeter length L_p divided by its size or diameter L [10]. This number S has a direct physical significance: it really measures the screening efficiency of the irregularity of the structure for Dirichlet Laplacian fields. Whatever the geometry, if the active zone has a size L , then as $L = L_p/S$ the factor $1/S$ can be considered to be the "screening efficiency" of the primary current distribution due to the geometrical irregularity. This is the physical significance of Makarov's theorem.

This result cannot be applied as such to an electrochemical cell because the boundary condition on the electrode is not $\mathbf{V} = 0$ but $\mathbf{V}/\nabla_n \mathbf{V} = \Lambda(s)$. We are then in the situation known as the secondary current distribution in electrochemistry. The real boundary condition introduces the physical scale Λ in the problem. The procedure that was proposed in [3] is to switch from the real geometry obeying the real boundary condition to a coarse-grained geometry obeying the Dirichlet boundary condition, with the coarse-graining depending on Λ . In a second step one can use the screening efficiency of the coarse-grained geometry to find the active zone of the electrode, hence its impedance. The discussion that we give now is a generalization of this procedure as it was proposed in references [3–5].

We allow for the general situation where the surface resistivity r is a function $r(s)$ of the curvilinear coordinate s . This is what we call the non-homogeneous linear case. In order to obtain quantities which can be compared to measurements made on real electrochemical cells [11] we introduce b which represents the thickness of the cell along the third dimension. We consider a region of perimeter ds around the curvilinear coordinate s . It presents an elementary admittance $Y_{\text{surf.}} = [b/r(s)]ds$ which is smaller than the "local access admittance" of order b/ρ . We call "local access admittance" the admittance of the small bulk area which is in front of this part of the interface. The value of this local access admittance does not depend on the area size since the admittance of a square of electrolyte with thickness b is equal to $Y_{\text{acc.}} = b/\rho$ whatever its size.

One can then consider a larger region between curvilinear abscissa s_1 and s_2 . Depending on s_1 and s_2 there exist two situations: if the curvilinear distance between s_1 and s_2 is small, the current is limited by the surface impedance. On the contrary, if this distance is large enough, the current is limited by the bulk resistance to access the surface. But in the latter situation we are, in a first approximation, back to the case of a pure Laplacian field with the boundary condition $\mathbf{V} = 0$ since it is the access to the surface that limits the current.

The idea then consists in coarse-graining locally the real geometry to a scale such that the perimeter L_{p1} in a region of size (or diameter) $L_{c\text{g},1}$ is given by the condition that the integral of $[b/r(s)]ds$ along that part of the perimeter is equal to the access admittance $Y_{\text{acc}} = b/\rho$. Equivalently the integral of $ds/\Lambda(s)$ over that same region should be equal to 1. Since such a definition of the coarse-grained diameter is difficult to implement computationally, we use instead the "local" chord between the curvilinear coordinates $s_1 = s - \Lambda(s)/2$ and $s_2 = s + \Lambda(s)/2$. The chord length $L_c(s)$ is thus defined as the distance between s_1 and s_2 in real space. In the case where r is a constant, independent of s , the above relation expresses simply that the curvilinear distance (or perimeter length) between s_1 and s_2 is equal to $\Lambda = r/\rho$.

Because of its definition, such a region can be considered as working uniformly. At the same time, in the new coarse-grained geometry, we are dealing with a pure Dirichlet Laplacian

field. We then shift from the real geometry to the coarse-grained geometry which is made of successive chords $L_c(s_1, s_2)$, $L_c(s_2, s_3)$, $L_c(s_3, s_4)$. In the coarse-grained geometry the curvilinear coordinate is named s' , as indicated in Figure 1b. The perimeter of the coarse-grained electrode is named $L_{p'}$. Each element or grain of the coarse-grained system presents an admittance which is equal to b/ρ so that the differential admittance of an element ds' is equal to $[b/\rho L_c(s')]ds'$. If there was no screening, the total coarse-grained electrode would be working uniformly and its admittance would be

$$Y_{cg, no\ screening} = \int_{cg} [b/\rho L_c(s')] ds' \tag{3}$$

where the integral is taken along the coarse-grained geometry. But due to electric screening there exist an active zone, where most of the current arrives and a passive zone with receives only little current [11, 12] so that the integral can be split in:

$$Y_{cg, no\ screening} = \int_{cg, active} [b/\rho L_c(s')] ds' + \int_{cg, passive} [b/\rho L_c(s')] ds' \tag{4}$$

The electrode admittance Y_{ode} is simply

$$Y_{ode} = \int_{cg, active} [b/\rho L_c(s')] ds' \tag{5}$$

Note that the integrand is only a function of the distribution of $r(s)$. The admittance does depend on the Laplacian field distribution only through the determination of the active zone. Calling L_{act} . the length of the active zone of the coarse-grained electrode, the above integral can be written

$$Y_{ode} = L_{act} \cdot [b/\rho] \int_{cg, active} [1/L_c(s')] (ds'/L_{act}) \tag{6}$$

The integral represents the harmonic mean of $L_c(s')$ along the active zone. We define $\langle L_c \rangle_{act}$. as:

$$\langle L_c \rangle_{act}^{-1} = (1/L_{act}) \int_{cg, active} ds'/L_c(s') \tag{7}$$

Our essential hypothesis, using an abrupt form of Makarov's theorem, is that the active zone have a size L_{act} . of the order of the size of the electrode L . The admittance takes then the very simple expression

$$Y_{ode} = (b/\rho)(L/\langle L_c \rangle_{act}) \tag{8}$$

This expression is universally valid. At this stage the problem has been simplified without any loss of generality but still requires to find the active zone of the coarse-grained electrode in order to compute $\langle L_c \rangle_{act}$. from equation (7).

One can go one step further for the wide variety of systems for which one can approximate the harmonic mean on the active zone by the value of the harmonic mean on the entire electrode, namely

$$\langle L_c \rangle_{act}^{-1} \approx \langle L_c \rangle^{-1} = (1/L_{p'}) \int_{cg} ds'/L_c(s') \tag{9}$$

Due to the fact that the harmonic mean is dominated by the small values of $L_c(s')$, this approximation is valid unless the smallest values of the chord length L_c are found only in the non-active region of the electrode. A counter-example to equation (9) could then be the special case of deep fjords with narrow access channels and small values of L_c only at the bottom of the fjords. Note however that equations (7, 8) are still valid in this case.

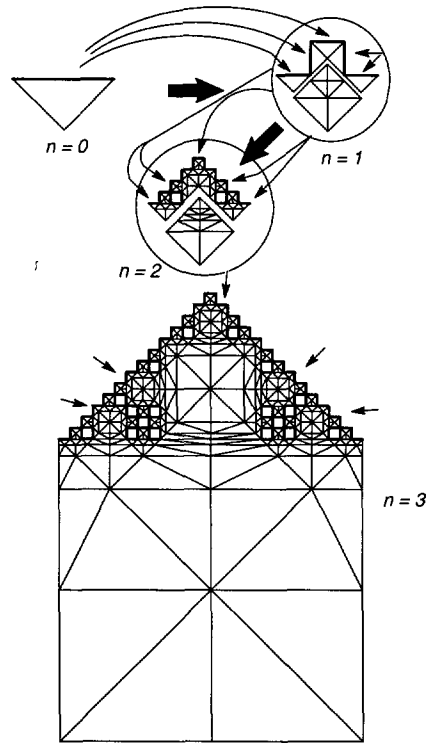


Fig. 2. — Fractal mesh used in the finite element computation. The figure presents the hierarchical construction of the mesh skeleton at a given generation. This mesh skeleton will be the basis of a set of meshes at this generation. Here the building of a third generation mesh skeleton is shown.

In all other cases the harmonic mean of the chord length will be the same if taken along the active zone or along the total coarse-grained structure. The admittance is now

$$Y_{\text{ode}} = (b/\rho)(L/\langle L_c \rangle). \quad (10)$$

We then obtain a very simple statement: the impedance of an irregular electrode in $d = 2$ is simply the square impedance ρ/b of the electrolyte divided by the number of chords needed to measure the size (or diameter) L of the electrode. This apparently simple result is not trivial. It expresses how the resistance of the electrode depends on the electrolyte resistivity and an average chord length corresponding to a perimeter of length $\Lambda(s)$. The geometry enters here through the relation between a perimeter of length $\Lambda(s)$ and its associated chord.

As there exists an exact mapping between s and s' , such that $ds'/L_c(s') = ds/\Lambda(s)$, the average chord length given by equation (9) can be written also, working on the initial non coarse-grained geometry

$$\langle L_c \rangle = \frac{\int L_c(s) ds / \Lambda(s)}{\int ds / \Lambda(s)}. \quad (11)$$

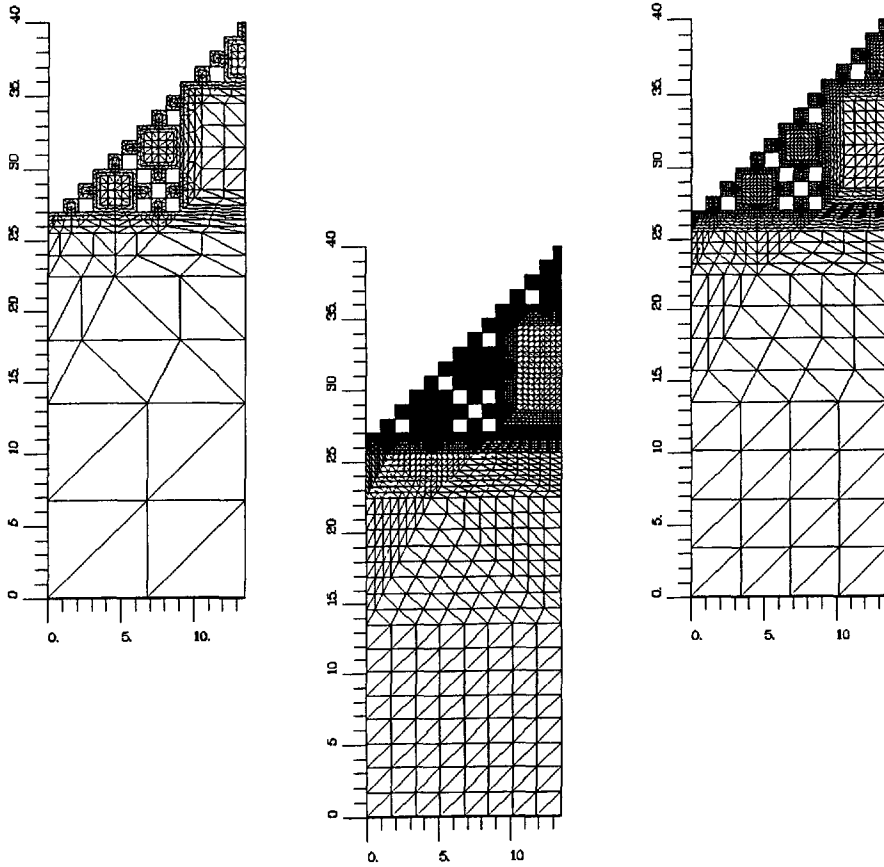


Fig. 3. — Example of different meshes at a given generation (here the third). The initial skeleton is refined by splitting each triangle in 4 identical triangles (by joining the middle of the sides of the initial triangle). Each mesh represents a new iteration of this operation.

Note that in the case of a flat but non-homogeneous electrode, the local chord length L_c is equal to $\Lambda(s) = r(s)/\rho$ and equations (8, 9) give:

$$Y_{ode} = (b/\rho)(L/L_p) \int ds/\Lambda(s) = b \int ds/r(s) \tag{12}$$

since $L = L_p$ for a flat electrode. We then recover the known value of the electrode admittance for $\rho = 0$. In the following we will test the validity of this approach in different cases.

Numerical Method

The electrode impedance Z_{ode} is obtained by $Z_{ode}(r) = Z_{cell}(r) - Z_{cell}(r = 0)$ which corresponds to the quantity measured in impedance spectroscopy. Numerical solution of the Laplacian problem is performed by using a finite element method rather than a finite difference scheme

for efficiency and accuracy purposes. This method will allow us also to extend later this study to non-linear regimes. The standard variational formulation of the problem is discretized with a triangular mesh and P_1 -Lagrange interpolation. The linear system obtained in such a way is solved by using the Cholesky method. To this end we use the Finite Element Library Modulef [13].

In order to compute the impedance of the irregular electrode with the greatest accuracy, we created a "fractal" triangular mesh of the structure (Figs. 2 and 3) which allows at the same time a detailed discretization of the boundary and an economic meshing in the bulk areas where the variations of the electrostatic potential are smaller. The mesh of the structure at generation $n + 1$ uses five times the mesh at generation n and a triangular mesh of the square placed under these five meshes (Fig. 2). The number of nodes of this meshing (which represents the number of degrees of freedom and thus the complexity of the problem) increases like 5^n where n is the generation of the fractal electrode, instead of 9^n in the case of a regular square mesh.

This method allowed us to compute accurately the impedance up to a 5th generation electrode on a standard Unix workstation (Hewlett-Packard C160). The computation time was from 1 second to a few minutes for a given value of the surface resistivity r .

Results

We compare now the land surveyor method with direct numerical simulation of the Laplacian field in the electrochemical cell. Several physical situations have been investigated.

The geometry of the electrode is given by the Viczek fractal (half of the domain described in Fig. 1). The bulk resistivity ρ is taken equal to 1 together with the smaller cut-off ℓ . A surface resistivity r equal to 1 corresponds then to $\Lambda = \ell = 1$. The geometry of the bulk electrolyte under the electrode is roughly a square and it has been numerically verified for various cases that the computation results do not depend on the distance between both electrodes as soon as it is greater than a few ℓ .

We first compute the response of the 4th generation electrode with a uniform surface resistivity r . In this homogeneous case it is well known that there exist two asymptotic behaviors for very small Λ (the Makarov regime for $\Lambda \ll 1$) and for very large Λ (the trivial uniform regime for $\Lambda \gg L_p$). In both regimes the electrode impedance is proportional to the surface resistivity r . Between these regimes, the impedance of a "fractal" electrode follows a power law whose exponent is approximately equal to the inverse of the interface dimension.

The results are shown in Figure 4. The general behavior of the land surveyor method reproduces the three regimes. The discrepancy that we observe for $\Lambda = r/\rho$ smaller than ℓ is due to an expected flaw of the finite elements simulation consecutive to insufficient mesh at the interface. This regime (the Makarov regime) would need a much finer mesh in order to be studied accurately. In this work we focus on the regime where $\Lambda = r/\rho > \ell$ which is the situation of practical interest. As shown in Figure 4, the "land surveyor method" is in good agreement with the numerical simulation. Not only it follows both power law for $\ell < \Lambda < L_p$ and $\Lambda > L_p$ regimes but it gives also the crossover between these regimes without more complex computation even though these crossovers extend over a large range of Λ . Note that the small oscillations in the land surveyor criterium are due to a peculiarity of our specific geometry: two points which are far along the electrode can be very near in the real space (this is the case for example when Λ is equal to the perimeter of a square, for example $\Lambda = 4\ell$ and $\Lambda = 20\ell$) leading to an artificial small value of $\langle L_c \rangle$. This divergence is not meaningful and could be avoided by using the diameter of the "grain" instead of the chord length. For all other tests

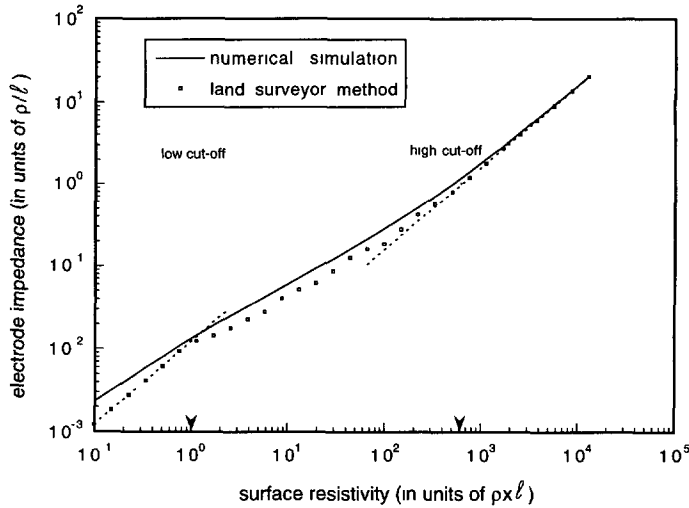


Fig. 4. — Comparison between the result of the “land surveyor method” and the numerical values of Z_{ode} for the 4th generation electrode. One can distinguish between three regimes (Makarov regime where $\Lambda \ll \ell$, intermediate regime where $\ell < \Lambda < L_p$, and purely ohmic regime where $L_p \ll \Lambda$), connected through two crossovers: one around $\Lambda = \ell$ and the other around $\Lambda = L_p$. Here $\ell = 1$ and $L_p = 625$.

and due to computation time considerations, the geometry of the irregular electrode will be a 3rd generation Viczek fractal.

The second test case is a study of a deterministic inhomogeneous distribution of the local resistivity $r(s)$. The resistivity r varies from r_{min} to $r_{max} = 10r_{min}$ along the curvilinear coordinate s of the interface going linearly from the minimum value (on the left edge of the interface) to the maximum value (in the middle of the interface) and then decreasing until the opposite edge. The comparison between the exact numerical simulation results and the land surveyor method is shown in Figures 5 and 6. In this case, the results of the land surveyor method match almost exactly the numerical simulation in all parts of the curve. The approximation (7) is extremely good since the harmonic mean of the chord length is dominated by the smallest values which are found in the active regions of the electrode.

We then study the opposite non-homogeneous case, where the minimum resistivity is located in the least accessible regions, here the upper region of the electrode. The ratio between r_{min} and r_{max} has been kept constant equal to 10. As expected, the land surveyor method fits the numerical simulation better in the large resistivity area of the curve. In the “fractal” or “power law” regime, the land surveyor method overestimates the admittance contribution of the low resistivity part of the interface, since this portion is partly screened. Nevertheless the ratio between both methods never exceeds a factor 2 which means that our criterium can still be used to determine the order of magnitude of the electrode impedance without any further computation. Note that, for this type of situation, it is possible to compute the Laplacian field on the new coarse-grained geometry to obtain the location of the active region and then use only the first part of equation (7). This would give a very good approximation of the electrode impedance at a minimum cost (solving numerically a Laplace equation with Dirichlet boundary conditions in a simplified geometry).

In the third case, Figure 7, we studied the validity of our method in the case of a random distribution of the resistivity along the interface, a most common case in real devices.

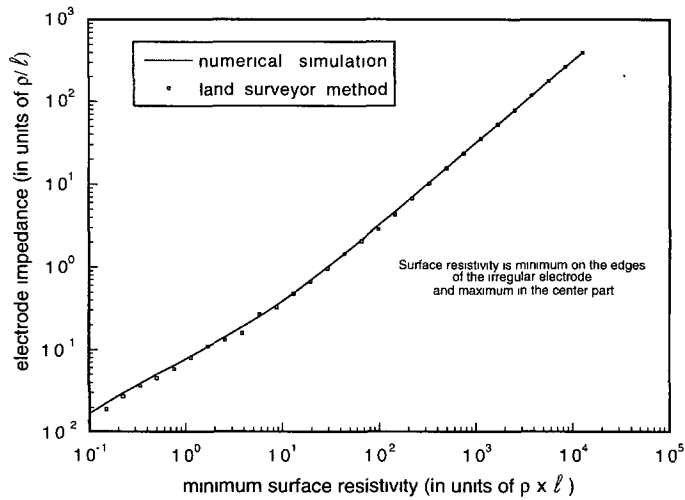


Fig. 5. — Comparison between the “land surveyor method” and the numerical simulation results for an inhomogeneous distribution of the resistivity along the electrode: the local resistivity is small on the lateral edges of the electrode and large in the middle part of the electrode. Note the perfect matching due to the good quality of approximation (7).

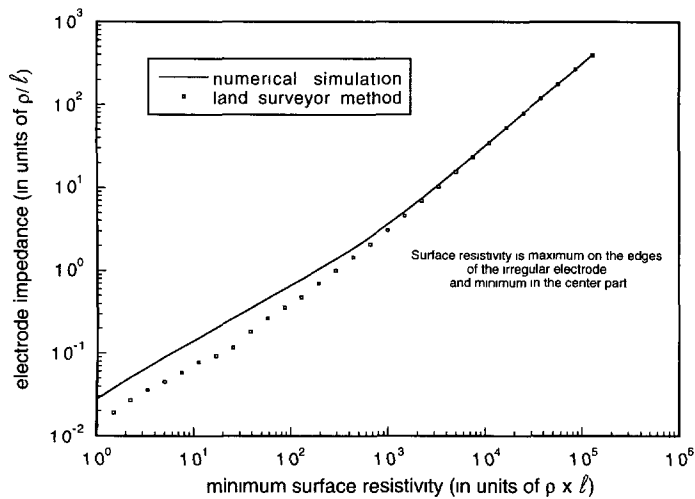


Fig. 6. — Comparison between the “land surveyor method” and the numerical simulation results for an inhomogeneous distribution of the resistivity along the electrode: the local resistivity is large at the edges and small in the middle part of the electrode. In this case the poor validity of approximation (7) leads to a significant discrepancy between both methods, but even in this case they never differ by more than a factor 2.

The ratio between maximum and minimum resistivity is kept equal to 10. As in the homogeneous case, results show very good agreement between numerical computation and the land surveyor method. This result was expected since the smallest values of the chord length are homogeneously distributed along the interface, in both active and passive regions.

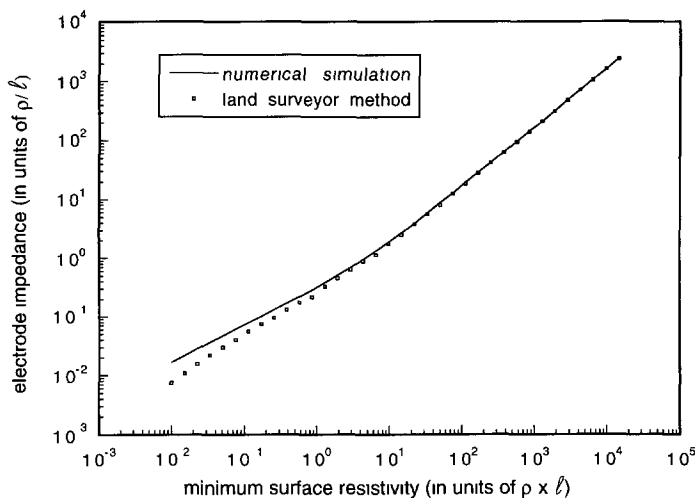


Fig. 7. — Comparison between the "land surveyor method" and the numerical simulation results for an inhomogeneous and random distribution of the resistivity along the electrode: as in the homogeneous case, the repartition of small resistivity values between active and passive regions of the electrode leads to a good matching between both methods.

Conclusions

In summary we have developed a new method of computing the transfer properties of irregular interfaces such as electrodes or rough absorbing membranes. Apart from the interface geometry, all that is needed are the values of the microscopic transport coefficients (here for instance the electrolyte resistivity and the Faradaic resistance). We have tested this method for various non-homogeneous distributions of the surface resistivity.

The general conclusion that one can draw from this work is that the measurement of the electrode impedance is a good approximate measurement of the harmonic average of the chord length corresponding to a perimeter $\Lambda(s)$. The simplicity of the method makes it a good candidate for the study of the response of irregular interfaces in non-linear regimes for instance when the local current across the electrode is related to the local voltage by a non-linear relation $\mathbf{j} = \mathbf{f}(\mathbf{V})$. All these results can be applied to the study of particle transfer across inhomogeneous and irregular porous membranes or catalysts as indicated in [1].

Acknowledgments

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