Electron Transfer through a Modified Electrode with a Fractal Structure: Cyclic Voltammetry and Chronoamperometry Responses

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The problem of charge transfer by electron hopping through a volumic-modified electrode with a fractal structure was addressed, both in the case of chronoamperometry and linear sweep voltammetry. A behavior intermediate between that seen in classical diffusion and that of a thin layer was found. The currents in chronoamperometry and the peak currents in cyclic voltammetry both depend linearly on a bilogarithmic scale with, respectively, the time and the scan rate. The slopes of the curves in both cases depend on the fractal dimension, provided the spectral dimension remains constant. Plots are given in the case where the spectral dimension is equal to 4/3.

Introduction

The field of modified electrodes, although active for ~20 years, continues to attract the attention of several scientists because of its numerous applications, particularly in the field of sensors.[1] Another field of renewed interest is establishing the relation between the electrochemical response of a volumic-modified electrode and its nanostructure, with the goal of gaining insight into the electrode material substructure. For example, the spatial distribution of the electroactive sites on the electrode material is expected to strongly influence the electrochemical response through the electron-transfer kinetics. In addition, close examination of the electrochemical response of a functionalized polymer is expected to give precious information about its structure. This approach has been introduced and used by us with functionalized conducting polymers[2−4] and recently with several sol−gel polymers,[5−10] for which the knowledge of the nanostructure is of great importance and often difficult to determine by other methods.

Analysis of the current recorded from a modified electrode with a homogeneous repartition of the redox sites has long been addressed by Andrieux and Savéant, who found that the electron transfer was diffusive-like, with an apparent diffusion coefficient $D = k\Delta x^2 C°$,[11] where $C°$ represents the concentration of redox sites, Δx is the average distance between two sites, and k is the isotopic rate constant inside the material (which is usually much different from its solution value). Further effort was made by Savéant to determine the role of k according to the polymer structure,[12] as well as the role of migration when it could occur.[13] However, no further effort was made to calculate the electrochemical response of modified electrodes with a particular, nonisotropic distribution of the electroactive sites. Here we address the problem of both a linear concentration variation inside a homogeneous electrode as well as the problem of electron transport in a fractal electrode; that is, an electrode with a fractal distribution of the redox sites.

Although the problem of diffusion toward an electrode with a fractal surface was addressed relatively early by several groups,[14−18] the problem of electron transfer in three-dimensional fractal electrodes (2 < df < 3) has not yet been addressed, probably because no examples of such electrodes were known. However, it is well known that inorganic silica xerogels and aerogels very often display such fractal structures, and the electrochemical behavior of a modified electrode prepared from a ferrocene functionalized xerogel exhibits quite anomalous behavior. These results will be discussed in light of the theoretical treatment presented next.

Results and Discussion

The problem of anomalous diffusion has been addressed by Alexander and Orbach,[19] who postulated that the number of sites visited was proportional to $t^{d_s/2}$, where d_s is introduced as the spectral dimension. On a fractal object, the number of accessible sites is proportional to r^{d_f}, where d_f is the fractal dimension and r represents the distance to an arbitrary origin. Therefore, the diffusion coefficient D is no longer independent of time, but depends on time according to the following law: $D \propto \langle r^2(t)\rangle/t \propto 1/t^{(1 - d_s/d_f)} \propto 1/r^{2(d_f/d_s - 1)}$, ($d_s/d_f$ being <1). We will use θ to represent the value $2(d_f/d_s - 1)$.

The problem that we address is the one of a modified electrode containing electroactive sites able to undergo fast electron exchange, with the charge-transfer kinetics obeying the Andrieux−Savéant−Laviron hypotheses and with a fractal instead of an isotropic distribution of the accessible sites. Therefore, we continue to postulate the invariance of the electron exchange rate constant k throughout the polymer, which constitutes a limiting hypothesis for the applicability of the model, as will be discussed later. The charge-transfer kinetics can now obey the equation $\partial C/\partial t = D(\delta/x)^{\theta}\partial^2 C/\partial x^2$, where the D of the isotropic case has been changed into $D(\delta/x)^{\theta}$, accounting for the fractal distribution. Here, δ represents the short distance cutoff length of the fractal structure, below which the system is again isotropic. This case also supposes that the electron exchange is not affected by the geometry of the

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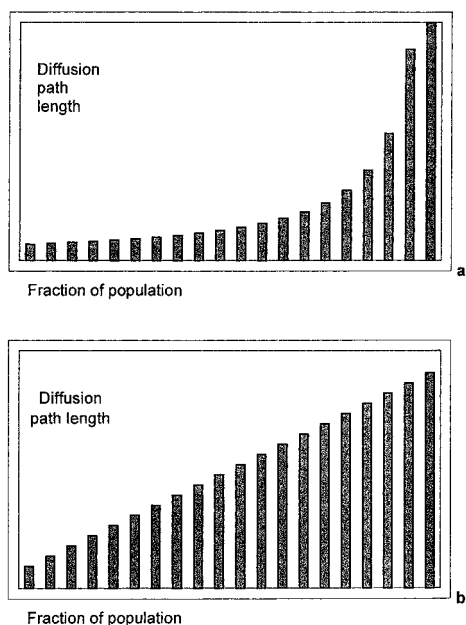
Figure 1. Model of the electrode structure representing the layers in each considered case: (a) fractal electrode (the last longest layer has been cut for reasons linked to the clarity of reading the scheme) and (b) classical compact triangular shaped electrode. Each bar represents the relative amount (in the whole modified electrode) of electroactive sites that are accessible through the as-defined pathway.

electrode because D varies as the charge-transfer rate constant inside the film and the average distance between neighbor sites.

This equation cannot be solved analytically, and for practical purposes linked with the solution of the electrochemistry problem, it is more convenient to come back to an intrinsic definition of the fractal sites distribution. Therefore, we express the fractal character of the electrode by postulating that classical diffusion takes place, but into an electrode constituted of a compact layer of length d, followed by a fractal layer containing fewer and fewer accessible sites, with the accessiblity of the sites depending on the pathway on the fractal. If we consider the diffusion-like[11] percolation of the electrons along a fractal, the average path within the fractal is $[\langle r^2(t)\rangle]^{1/2}$, which is proportional to $r^{-\theta/2}$. Therefore, it is equivalent to calculate the situation of an isotropic electron pseudo-diffusion in a structure with a pathway distribution varying as $d/y^{\theta/2}$ and having y vary between 1 and 0,[20] while retaining a homogeneous concentration of *accessible* electroactive centers (Figure 1a). For the sake of comparison with the nonfractal case, we have also calculated the behavior of electrodes with a special geometric triangular structure; in this case, a linear variation of the pathways with x is met within the electrode (as represented in Figure 1b, always keeping a homogeneous concentration of the accessible redox sites).

We can thus calculate the values of the current as a function of the time for a chronoamperometry experiment, as well as the peak currents as a function of the scan rate for cyclic voltammetry. As is usual in thse types of theoretical treatments, all parameters have been adimensionalized as detailed in the *Experimental Section.*

(1) Chronoamperometry. *(a) Case of a Nonfractal Variation of the Geometric Electrode Structure.* We have calculated the electrochemical responses of a modified electrode with the triangular channeled structure shown in Figure 1b. The chronoamperometry results (Figure 2) are displayed as a bilogarithmic plot. The data show that, in such a case, with the exception of very short times no linear dependence is found of the currents
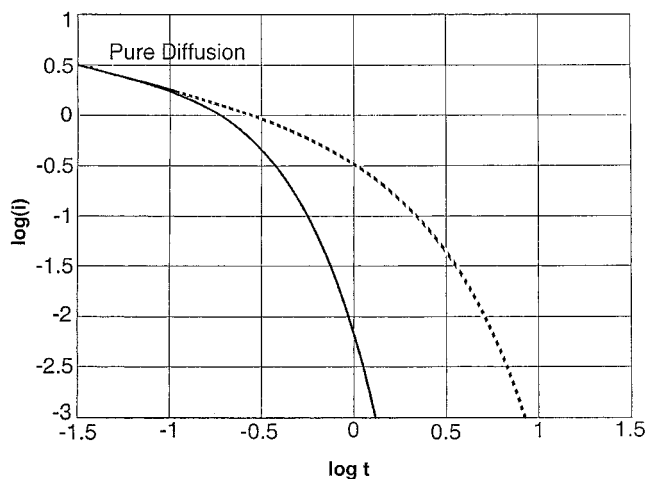

Figure 2. Bilogarithmic chronoamperograms for both a classical compact homogeneous electrode (full line) and the triangular shaped electrode of Figure 1a (dashed line).
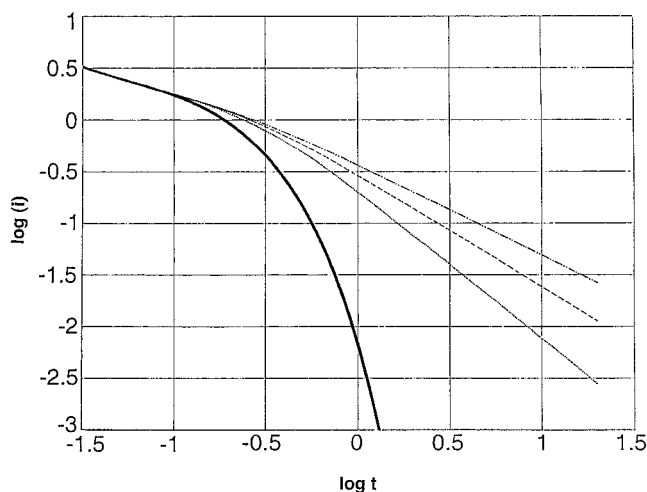
Figure 3. Bilogarithmic chronoamperograms for a classical compact layer (full line, as Figure 2) and fractal electrodes with three different fractal dimensions. Key: (dotted line) $\theta = 1$; (dashed line) $\theta = 1.6$; (mixed line) $\theta = 2.5$.

with time [at very short times, the classical (cottrellian, with a $^1/_2$ slope) is obtained because a compact first layer of definite length has been introduced (for sake of comparison with the following fractal model)]. We have verified that this lack of linear dependence of currents with time is always true with electrodes featuring other types of geometry with a definite predetermined shape. In all cases, only a more or less curved Cottrell plot is displayed, with the main differences arising from the length of the transition domain (which arise from the average depth through which the electrode is shaped).

(b) Case of an Electrode with a Fractal Distribution of the Electroactive Sites. The logarithmic plots arising from chronoamperometry experiments on a fractal electrode are shown on Figure 3 for different values of the θ parameter. It is clear that in all cases [except the situation at very short times; again a compact layer of definite thickness has to be introduced, within which a classical cottrellian diffusion (characterized by the $^1/_2$ slope) is encountered; however, in the case of the fractal model, this length has to be introduced (otherwise the calculation is no longer feasible) and it corresponds to the short cutoff length of the fractal]. New straight plots are obtained, but the slope of the plots deviates noticeably from 0.5 to higher values as a consequence of the more and more difficult access to the sites.
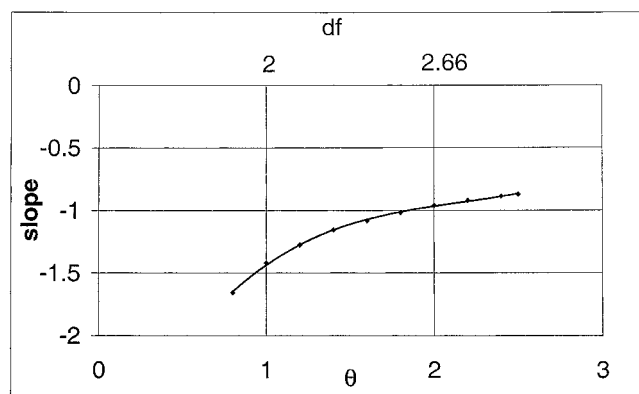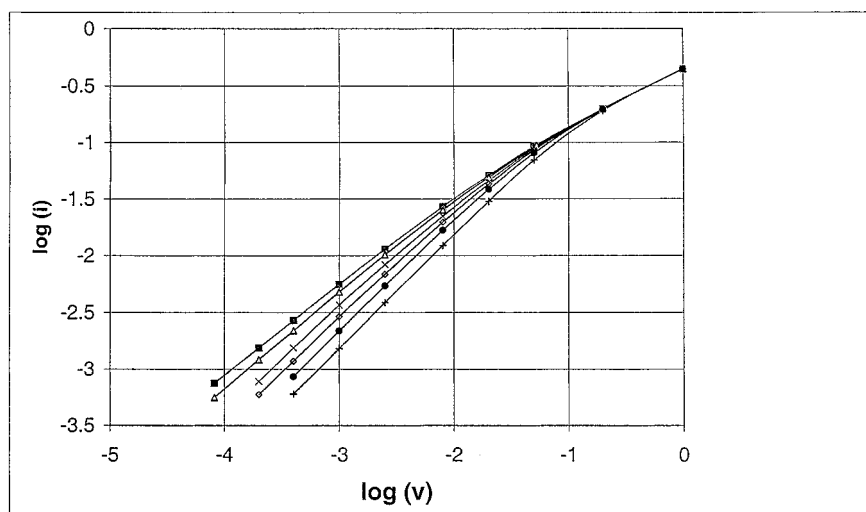
Figure 4. Dependency of the slopes of the curves represented in Figure 3 with both the exponent θ and the fractal dimension d_f. The slope was calculated on the pseudolinear part of the curve on Figure 3, corresponding to the positive values of log (t).

If we admit that d_s is equal to 4/3, as previously postulated[19] (even in cases where d_s would be different, its value is certainly very close[19,21]) and that d_f is necessarily to be taken between 2 and 3, it is possible to determine a reasonable interval for θ. This approach allows θ to vary between 1 and 2.5, with outer values being deprived of physical meaning. Within this range, the slope of the pseudo-Cottrell plots vary between 1.42 and 0.87, the lower values being expected to be obtained in the case

of the higher fractal dimensions. However, the upper limit is not 0.5, showing that there is no continuity with the isotropic case.

Figure 4 shows the dependence of the slopes on both θ and d_f (because these parameters are linearly correlated). Because the curve is monotonic, it is clear that chronoamperometry on functionalized materials can be a useful tool to determine the fractal dimension of the modified electrodes. However, the determination of the slopes requires the use of a very long time range, which is usually beyond the capability of the apparatus. However, making several potential step experiments may cause changes in the electrode and increase the uncertainty of the measurements. Therefore, we chose to check if linear scan (or cyclic) voltammetry could also be modeled and used for such purposes.
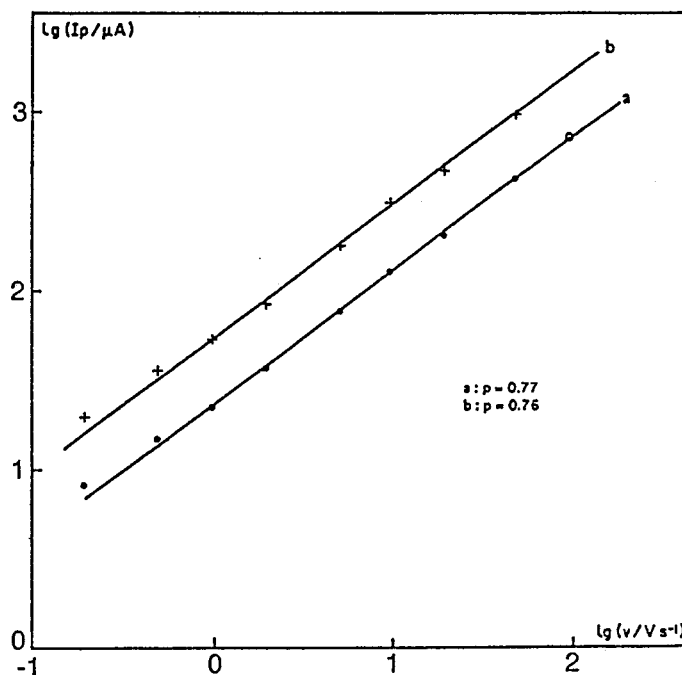
(2) Cyclic Voltammetry. Figure 5 shows the normalized peak currents dependence on the scan rate with the same fractal electrodes. Again, a logarithmic straight plot is obtained, and, as previously noted, the slope differs from the 0.5 value obtained for classical diffusion into a compact structure. This time, the slopes are of course taken between 0.5 and 1, which constitute, respectively, the case of classical diffusion and the case of a monolayer without transport. Figure 6 gives the dependence of the slopes of the log i/log v plots, both according to the θ and d_f values. Again, knowledge of the plots can give access with reasonable precision to the fractal dimension of the modified electrode. Because cyclic voltammetry is more convenient and

Figure 5. Bilogarithmic plot of the peak currents (defined as in the experimental part) with the scan rate for several values of the exponent θ. Key: (■) $\theta = 2.5$; (△) $\theta = 2$; (×) $\theta = 1.4$; (◊) $\theta = 1$; (●) $\theta = 0.6$; (+) $\theta = 0$ (thin compact layer, slope equal to 1).
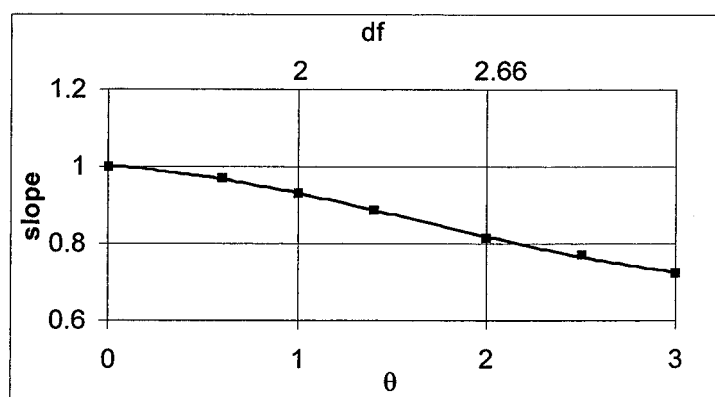
Figure 6. Dependencies of the slopes of the curves represented Figure 5 with both the exponent θ and d_f. The slope was calculated on the pseudolinear part of the curve on Figure 3, corresponding to the log (v) values inferior to −2.2.

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Figure 7. Dependencies of the peak currents with the scan rate for two modified electrodes made from co-gels of silica, prepared from the sol−gel copolymerization of tetramethoxysilane and ferrocene functionalized by two triethoxysilyl moieties, according to ref 22: (a) co-gel prepared from a 50%/50% mixture, and (b) co-gel prepared from 75% tetramethoxysilane and 25% functionalized ferrocene.

precise than chronoamperometry, this method is more practical; however, the range of slopes is narrower in this case, which requires good precision of the measurements. It should be remarked that again, although the classical thin layer case is met when $d_f = 4/3$ ($\theta = 0$), the curve appears to be asymptotic to a value close to 0.7, even for d_f values >3, which have little physical meaning. It is not obvious why the limit is not the classical diffusion case.

Finally, we should indicate that, like chronoamperometry, no other electrode geometry gives straight plots for such a dependence. For example, with the triangular distribution of the pathways, as in the electrode in Figure 1, only a less bent and wider borderline is obtained between the diffusion (slope 1/2) and the adsorbed layer (slope 1) cases.

(3) Application to the Determination of the Fractal Dimension of Functionalized Silica. Cogels prepared by the sol−gel copolymerization of tetramethoxysilane and a trimethoxysilane functionalized ferrocene were used to prepare hybrid-modified electrodes. In the case of monofunctionalized ferrocene, the electrodes exhibited an odd behavior, both in cyclic voltammetry and chronoamperometry.[22] The Figure 7 represents the bilogarithmic dependence of the peak currents on the scan rates in cyclic voltammetry. It is clear that exactly the same behavior as the one shown in the previous theoretical framework is evident and that two of the cogels display slopes in the expected range for a fractal structure of the electrode. The fractal dimension of the cogels appears relatively independent of the concentration of ferrocene when the latter is relatively high. From comparison with the data in Figure 6, we can therefore determine the d_f value of this ORMOSIL[23] to be ∼2.8−3. Unfortunately, this value is in the range of highest uncertainty regarding the d_f determination.

It should also be mentioned that the experimental curves do not indicate the existence of the transition compact−fractal layer, which has been introduced in the previously discussed theoretical model. This result is probably because the compact layer (equivalent in our treatment to the short cutoff length of the

fractal) is very small, and the shorter times investigated in our cyclic voltammetry experiments are too long. In fact, the highest scan rate used in our experiment, 100 V/s, corresponds to an average corresponding characteristic distance of 10 to 30 nm (on the basis of the average D values measured in functionalized silicas[22]). This length is probably at best of the same order of the cutoff length as the fractal, and therefore the transition is not visible. The reliable use of higher scan rates is rendered very difficult by the remaining ohmic drop in the modified electrodes.

Finally, it should be reported that when the ferrocene dilution inside the silica is quite low, anomalous peak current−scan rate dependencies are again found, but with slopes closer to 0.5.[21] In such cases, the hypothesis of the constancy of D is probably no longer valid, given that the rate constant for electron exchange in the films is probably subjected to important local changes, which runs out our former hypothesis on the analysis.

Conclusion

We have shown that the determination of both the chronoamperometry and cyclic voltammetry responses of a volumic-modified electrode with a fractal repartition of the accessible electroactive sites was possible. Bilogarithmic plots of both the currents versus time in chronoamperometry and the peak currents versus scan rate in cyclic voltammetry are linear, and the slope of the curve is related to the fractal dimension of the electrode provided that the spectral dimension does not vary. On the basis of a spectral dimension equal to 4/3, the fractal dimension can be extracted from experimental data, which has been done in the case of silica ORMOSILS.

It should be emphasized that this linear dependence appears to be specific to the electrode fractality, whereas other continuous electrode geometries lead to more or less curved plots with no clear-cut shape. Such linear bilogarithmic straight plots with slopes different from 0.5 or 1 are unprecedented in electrochemistry and could open the way to the analysis of new modified materials.

Experimental Section

All the symbols not clearly defined are supposed to have their usual meaning in classical electrochemistry.

Calculation Procedures. For both potentiostatic chronoamperometry as well as linear sweep voltammetry, calculations were made on a distribution of layers with thicknesses defined as in Figure 1, the total current response being the sum of each layer response. The only difference from Figure 1 is that the number of layers chosen for calculations was usually 40. In each layer, quasidiffusion occurs with an initial concentration $C°$ of the redox sites.

The equation that is solved inside each layer of thickness d is the following: with the following conditions: $t = 0$; when 0

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

$< x < d$, $C = C°$; when $x > d$, $C = 0$; and $(\partial C/\partial x)_d = 0$. The current is given by $I = FS\sqrt{D}(\partial C/\partial x)_0$.

Chronoamperometry. At $t = 0$ the concentration at the electrode becomes 0. Taking into account the adimensionalized parameters: with

$$\tau = \frac{t}{t°} \text{ where } (t° = \text{max time}); \; a = \frac{C}{C°}; \; y = \frac{x}{\sqrt{Dt°}}; \; \delta =$$

$$\frac{d}{\sqrt{Dt°}}. \text{ The equation to solve becomes } \frac{\partial a}{\partial \tau} = D\frac{\partial^2 a}{\partial y^2}$$

$\{\tau = 0, 0 < y < \delta: a = 1\}$; $\{\tau > 0, y = 0: a = 0\}$; and
$$\{\tau > 0, y = \delta: (\partial a/\partial y) = 0\}.$$

Calculation by an explicit method[24] is conducted with 10 points on the layer corresponding to the smaller thickness layer (cutoff length) with $\Delta\tau/\Delta y^2 = 0.45$. For example, in the calculation for Figure 2, $\Delta t = 0.000125$ s and the figure is drawn for $t° = 20$ s.

Linear Sweep Voltammetry. In linear sweep voltammetry, the adimensionalized parameters are, as usual:[25]

$$\tau = Fvt/RT, \; a = C/C°, \; y = x\sqrt{Fv}/\sqrt{RTD}, \; \xi =$$
$$-F/RT(E - E_0), \; \tau = \xi + u_i, \text{ and } \psi = i/FSC°\sqrt{D}\sqrt{Fv/RT}.$$

The calculation needs 20 points in the cutoff layer from $\xi = -u_i = -10$ to $\xi = +10$. The peak current ψ_p is calculated for several values of the parameters. For large values of Δy (such as $\Delta\tau/\Delta y^2 = 0.45$, large values of $\Delta\tau$, large values of sweep rate), a diffusion-like curve is obtained as indicated by a value of $\psi_p = 0.446$. Small values of Δy lead to voltammetric curve displaying a partial character of adsorption.[11] The curves presented in Figure 5 are normalized for a maximum value of v where diffusion is reached. The current i corresponds to $\sum\psi_p\sqrt{v}$ on the 40 diffusion layers on which the calculations are made.

Preparation of the Functionalized Xerogels. The xerogels were prepared by co-condensation of trimethoxysilylferrocene (TMSFc) and tetramethoxysilane (TMOS), base catalyzed. The following procedure was typically followed: x mmols of TMSFc and y mmols of TMOS (typically in the 0.2−1 mmol range) were dissolved in 10 mL of methanol, and 5 molar equivalents

of water and 10^{-3} equivalents of ammonium fluoride, relative to the global Si amount, were added. The liquid sol was rapidly stirred for 1 min, and then spun for 5 min on a 2-mm diameter platinum electrode (previously carefully cleaned with a 1/1/1 mixture of nitric, sulfuric, and chlorhydric acids) at ∼1000 rd/s, which caused its immediate gelation. After drying (1 week), a completely stable xerogel state was reached and the electrode was transferred into a classical electrochemical cell, filled with acetonitrile/0.1 M tetraethylammonium perchlorate electrolyte, and cycled with homemade electrochemical equipment that was fitted for fast electrochemistry with an ohmic drop compensation system.[6,9,22] On the basis of a complete condensation, the relative concentration of ferrocene in the resulting xerogel can be estimated; in the case of curve a, Figure 7, the ferrocene concentration in the (solid) xerogel was 3×10^{-3} mol/cm^3, and in the case of curve b, it was 1.3×10^{-3} mol/cm^3.

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(20) Note that in this description, the fractal cutoff lenth (at short distances), δ, is nessecarily larger than d, but not obligatorily equal to d. Note also that it is not necessary to define a long-range cutoff distance of the fractal, the latter being naturally introduced by the number of divisions used for the computation (in our case 40); this length is therefore, in our case, equal to 40d.

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