Chapter 2

Theory of Absorbance-Transients of a Redox Reaction at an Optically Transparent Rough Electrode
Abstract

Theory for the potentiostatic absorbance-transient for a species generated at the rough electrode-electrolyte interface is developed. Absorbance-transients are strongly affected by electrode geometries, particularly the effect of electrode roughness which is the least understood area, is dealt here. A general operator structure between concentration, surface absorbance density, absorbance transients and arbitrary roughness profile of electrode is emphasized. The statistically averaged absorbance-transients are obtained by ensemble averaging over all possible surface roughness configurations. An elegant mathematical formula between the average spectroelectrochemical absorbance-transient and surface structure factor or power-spectrum of roughness is obtained. This formula is used to obtain an explicit equation for the absorbance on an approximately self-affine (or realistic) fractal and non-fractal electrode. Our results are also applicable to chronocoulometric response as it’s directly related to chronoabsorptometric response. Limiting behavior in short time is attributed to the electrode roughness factor and surface curvatures. Limiting behavior in long time is like a smooth electrode response but the transition region is attributed to the mean square width of roughness. In the intermediate time, the absorbance has anomalous power law behavior which is attributed to the diffusion length weighted spatial frequency features of roughness and becomes almost time independent for large roughness electrodes. Finally, this theory provides a quantitative description of the role of roughness on potential step transmission chronoabsorptometry and chronocoulometric measurements, therefore opening up the way to explore and understand various anomalies in their response.
1 Introduction

Spectroelectrochemistry (SEC) is an important technique to identify reaction intermediates, products, mechanisms and other electron transfer processes taking place at an electrode-electrolyte interface [1, 2, 3, 4]. The main motivation of this technique has been to provide means for obtaining information about spectroelectrochemical systems that could not be gathered by either purely electrochemical or spectrochemical methods. Kuwana et. al [5] was the first group who monitored the course of an electrochemical reaction by transmission spectroscopy for diffusion controlled reaction in 1964. His group was main contributor towards the development of this important research field [6, 7, 8, 9, 10, 11, 12, 13]. This technique is used to analyse various systems like optically transparent minigrid electrode [14], current step spectrochemical relations for diffusion [15], potential step transmission chronoabsorptometry [16], absorbance measurements by the reflected light [17], microelectrode [18], electrochromic effects and devices [19, 20, 21, 22, 23, 24, 25], carbon nanostructures [26], graphene [27], metal clusters [28, 29, 30, 31, 32], and biomolecules [33, 34, 35, 36]. Optically transparent electrodes (OTEs) are valuable platforms for a broad range of applications stemming from fundamental spectroelectrochemical investigations of electron transfer mechanisms to applied technological applications [27].

For the redox reaction \( O + ne^- \rightleftharpoons R \) taking place at an electrode-electrolyte interface, by using Beer-Lambert and Faraday’s laws we can find the concentration and charge (chronocoulometrically), respectively. The combination of these two laws gives relationship between charge and absorbance, that is, the absorbance is proportional to the amount of charge transfered [37]. If the wavelength is such that one of the species (reduced or oxidized) absorbs light in the UV-visible region then, change in absorbance with time can be monitored spectroelectrochemically. In general, the chronocoulometric charge and the absorbance transient of species are related as:

\[
\mathcal{A}(t) = \frac{\epsilon Q(t)}{nFA_0},
\]

where \( \mathcal{A}(t) \) is the absorbance, \( \epsilon \) is the molar absorptivity of reduced (photoactive) species, \( n \) is number of electron(s) involved in the reaction, \( F \) is Faraday
Figure 2.1: Schematic diagram of diffusion controlled charge transfer at rough optically transparent electrode (OTE) where the charge transfer reaction $O(sol) + ne^- \rightarrow R(sol)$ under Nerstian condition is coupled to the bulk diffusion of oxidized or reduced species. The rate determining step is diffusion. Here detector is spectrophotometer. The various morphological characteristics which control the spectroelectrochemical responses of electrode-electrolyte interface such as lower ($l$) and upper ($L$) cutoff length scales of fractality, width ($h$) and diffusion length ($\sqrt{Dt}$).

constant, $A_0$ is the projected area of the electrode, $Q(t)$ is the charge and $t$ is the time. Equation 1.0.1 interrelates two important techniques which are experimentally different. The absorbance for the diffusion-limited processes at optically transparent planar electrode is given by [2]

$$A_P(t) = \frac{2 \epsilon C_O^0 \sqrt{Dt}}{\sqrt{\pi}}, \quad (1.0.2)$$

where $A_P(t)$ is the absorbance for the smooth optically transparent planar electrode, $C_O^0$ is the concentration of the oxidized species (if reduced species is absorbing) and $D$ is the diffusion coefficient.

Most of the real surfaces are not smooth. So, the study of geometrical (roughness) aspects of the electrode (here OTE) is of practical importance since roughness affects the spectroelectrochemical response like current, charge, impedance,
absorbance etc. The recent interest in realistic fractal geometry and methodology used for its characterization has opened a new window to understand the influence of surface disorder. This includes potential sweep methods on an arbitrary topography [38], Cottrellian current at rough electrode with solution resistance effect [39], partial diffusion-limited interfacial transfer/reaction [40, 41], Gerischer admittance at rough electrode [42], anomalous Warburg impedance at rough electrode [43, 44, 45] and anomalous diffusion reaction rates or diffusion controlled potentiostatic current transients [46, 47, 48, 49, 50, 51]. In this chapter also, we wish to use same approach to characterize the rough OTE in relation to the diffusion-limited reversible redox reactions taking place at the electrode-electrolyte interface through absorbance transients. Fig. 2.1 depicts the rough OTE with emphasis on morphological and phenomenological scales which control the spectroelectrochemical response of such electrode-electrolyte interface.

This chapter is organized as follows: we formulate the problem and solve it for the arbitrary profile of the electrode by using a perturbation method. The absorbance transient is obtained for the surfaces with known profile as well as with random roughness profiles. Results for the absorbance-transient are analysed for self-affine fractal surfaces and non-fractal surfaces. Finally, results, discussion and conclusions are reported.

2 Formulation

The total absorbance $A(t)$ for diffusion controlled processes under single potential step experiment ($\delta E(t) = E - E^0$; where $E$ and $E^0$ is the applied potential and formal potential, respectively), for an interfacial redox reaction, $O + ne^- \rightleftharpoons R$, can be obtained by solving appropriate diffusion equation. The concentration profile $C_i(\vec{r}, t)$, satisfies the diffusion equation as follows:

$$\frac{\partial}{\partial t} C_i(\vec{r}, t) = D_i \nabla^2 C_i(\vec{r}, t),$$

(2.0.1)

where $i \equiv O, R$ representing the oxidized or reduced species, $\delta C_i(\zeta)$ is the difference between surface and bulk concentration, $D_i$ is diffusion coefficient (for
simplicity we assume \( D_O = D_R = D \) and \( \vec{r} \) is the three dimensional vector, \( \vec{r} \equiv (x, y, z) \). There is a local transfer kinetics limitation at the interface \((\zeta)\) which in general is represented by the Nerstian boundary condition

\[
\delta C_O(z = \zeta(\vec{r}), t) = -\frac{C^0_O - C^0_R \theta}{1 + \theta} = -C_s, \tag{2.0.2}
\]

where \( \theta = \exp(-nf(E - E^{0}')) \) and the \( \delta C_O(t) \) is a function of the impressed potential, through Nernstian assumption and \( f = F/RT \) where \( F, R \) and \( T \) have usual meanings. At initial time, and far off from the interface a uniform initial and bulk concentration \((C_i^0)\), is maintained, viz, \( C_i(\vec{r}, t = 0) = C_i(Z \to \infty, t) = C_i^0 \). Since at initial times, only oxidized species is present so \( C_R^0 = 0 \) and the above Eq. 2.0.2 becomes \( \delta C_O(z = \zeta(\vec{r}), t) = -\frac{C^0_O}{1+\theta} = -C_s \). For backward reaction, if oxidized species is light absorbing, under this condition initially \( C_O^0 = 0 \) then the above equation will be \( \delta C_O(z = \zeta(\vec{r}), t) = \frac{C^0_R \theta}{1+\theta} = -C_s \). If potential is large enough (diffusion-limited case) then, \( \theta = 0 \) and it is reduced to \( \delta C_O(z = \zeta(\vec{r}), t) = -C^0_O = -C_s \). We wish to develop a perturbation solution in boundary profile of this boundary-value problem for a deterministic as well as random roughness geometry.

Now, using Fick’s first law, the important and observable quantity that is, the local absorbance density \( \alpha(t) \), upto time \( t \) is given by

\[
\alpha(z = \zeta(\vec{r}_i), t) = \frac{\epsilon D}{A_0} \int_{0}^{t} \partial_{n} \delta C_O(z = \zeta(\vec{r}_i), t') dt', \tag{2.0.3}
\]

The local absorbance density Eq. 2.0.3 is nothing but the time integral of flux which gives the total amount of the photoactive species generated multiplied by molar absorptivity of that species. Therefore, the total absorbance over surface
\( \zeta(\vec{r}_\parallel) \) at the interface upto time \( t \) is given by

\[
A(t) = \frac{\epsilon D}{A_0} \int_0^t \int_{S_0} dS_0 \beta \partial_n \delta C_0(z = \zeta(\vec{r}_\parallel), t') \, dt'
\]

\[
= \int_{S_0} dx \, dy \beta \alpha(z = \zeta(\vec{r}_\parallel), t),
\]

(2.0.4)

where \( \hat{n} = (1/\beta)(-\nabla_\parallel \zeta(\vec{r}_\parallel), 1), \nabla_\parallel = (\partial/\partial x, \partial/\partial y) \) and \( \partial_n = \hat{n} \cdot \nabla \) signifies the outward drawn normal derivative at the surface. For calculating the absorbance at an electrode-electrolyte interface one needs to evaluate the concentration profile around an arbitrary rough electrode-electrolyte interface, as indicated through Eq. 2.0.4.

3 Perturbation Solution for an Arbitrary profile Electrode

The perturbative solution for the concentration profile can be written in Fourier and Laplace transform domains for a weakly fluctuating rough surface. Therefore, the concentration profile for a weakly fluctuating two-dimensional rough surface in Fourier and Laplace transform domains is written as [49, 50]:

\[
\delta C(\vec{K}_\parallel, z, p) = \left( -\frac{C_0}{p(1+\theta)} \right) \exp(-q_\parallel z) \left\{ (2\pi)^2 \delta(\vec{K}_\parallel) + q \hat{\zeta}(\vec{K}_\parallel) + \hat{\chi} \hat{\zeta}(\vec{K}_\parallel - \vec{K}_\parallel') \hat{\zeta}(\vec{K}_\parallel') \right\},
\]

(3.0.1)

where \( \delta(\vec{K}_\parallel) \) is the two-dimensional Dirac delta function in Fourier transform wave vector \( \vec{K}_\parallel \), \( \hat{\zeta}(\vec{K}_\parallel) \) is the two-dimensional Fourier transform of the rough surface profile \( \zeta(\vec{r}_\parallel) \), \( \hat{\chi} \) is an operator which depend on phenomenological diffusion length \( (1/q = \sqrt{D/p}) \) and wave vector of surface roughness profile \( \vec{K}_\parallel \). The operator \( \hat{\chi} \) is defined as:

\[
\hat{\chi} = \frac{q}{2(2\pi)^2} \int d^2 K_\parallel' \left[ 2q_{\parallel,\parallel'} - q \right], \quad q_\parallel = \sqrt{p/D}, \quad q_{\parallel,\parallel'} = \left[ q^2 + |K_\parallel - K_\parallel'|^2 \right]^{1/2}, \quad p \text{ is Laplace transform variable and the magnitude}
\]
of wave vector, $K_{\parallel} = |\vec{K}_{\parallel}|$. Equation 3.0.1 is useful to predict concentration distribution around an arbitrary surface roughness profile under influence of single potential step function through $\theta(E) = \exp(-nf(E - E_{0}'))$. This can be achieved by taking inverse Laplace transform and inverse Fourier transform of Eq. 3.0.1 for a given roughness profile.

The local absorbance density (in Eq. 2.0.3), $\alpha(t)$, in Laplace and Fourier transformed domain for weakly and gently fluctuating two dimensional rough surface is obtained as:

$$\alpha(\hat{\zeta}, p) = \frac{e}{A_{0}} \left[ \hat{a}_{0}(2\pi)^{2} \delta(\vec{K}_{\parallel}) + \hat{a}_{1} \hat{\zeta}(\vec{K}_{\parallel}) + \hat{a}_{2} \hat{\zeta}(\vec{K}_{\parallel}' \cdot \hat{\zeta} (\vec{K}_{\parallel} - \vec{K}_{\parallel}')) \right],$$

(3.0.2)

where $\hat{a}_{0}$, $\hat{a}_{1}$, $\hat{a}_{2}$ are the operators for the smooth surface, first and second order terms in Laplace and Fourier transformed domain, respectively. These operators are functional of phenomenological diffusion length ($1/q = \sqrt{D/p}$), wave vector of surface roughness profile ($\vec{K}_{\parallel}$) and external perturbation potential ($E$); and are defined as follows:

$$\hat{a}_{0} = \frac{C_{0}^{0}}{q p (1 + \theta)}, \quad \hat{a}_{1} = \frac{C_{0}^{0}}{q p (1 + \theta)} (q_{\parallel} - q), \quad \text{and} \quad \hat{a}_{2} = \frac{C_{0}^{0}}{(2\pi)^{2} q p (1 + \theta)} \int d^{2}K'_{\parallel} \left[ q_{\parallel} q_{\parallel}' - \frac{1}{2} (q^{2} + q q_{\parallel}) - |\vec{K}_{\parallel} - \vec{K}_{\parallel}'|^{2} \right],$$

(3.0.3)

Therefore, the Laplace transformed absorbance at an arbitrary profile electrode is given by

$$A(p) = \frac{e}{A_{0}} \int_{S_{0}} d^{2}r_{\parallel} \left[ \hat{a}_{0}(2\pi)^{2} \delta(\vec{K}_{\parallel}) + \hat{a}_{1} \hat{\zeta}(\vec{K}_{\parallel}) + \hat{a}_{2} \hat{\zeta}(\vec{K}_{\parallel}' \cdot \hat{\zeta} (\vec{K}_{\parallel} - \vec{K}_{\parallel}')); \vec{K}_{\parallel} \rightarrow \vec{r}_{\parallel} \right],$$

(3.0.4)

where notation for the inverse Fourier transform is $\left\{ f(\vec{K}_{\parallel}); \vec{K}_{\parallel} \rightarrow \vec{r}_{\parallel} \right\} = \frac{1}{(2\pi)^{2}} \int d^{2}K_{\parallel} e^{j\vec{K}_{\parallel} \cdot \vec{r}_{\parallel}} f(\vec{K}_{\parallel})$ with $j = \sqrt{-1}$. $\hat{a}_{0}$, $\hat{a}_{1}$, $\hat{a}_{2}$ are the operators for the smooth surface, first and second order terms in Laplace transformed domain, respectively.
Operator $\hat{a}_2$ in Eq. 3.0.4 and $\hat{a}_2'$ in Eq. 3.0.3 differs only in coefficient of last term. The operator $\hat{a}_2$ is defined as follows:

$$
\hat{a}_2 = \frac{C^0_0}{(2\pi)^2 q p (1 + \theta)} \int d^2 K'_{||} \left[ q_{||} q_{||}' - \frac{1}{2} (q^2 + q q_{||}) - |\vec{K}|| - |\vec{K}'_{||}|^2 \right].
$$

Equation 3.0.4 can be used to predict absorbance after taking inverse Laplace transform and inverse Fourier transform for a known surface profile. This expression is very important to provide insights for the response of a nanometer to micrometer scales of a structured electrode which represents an arbitrary geometric profile or a rough electrode with known profile.

### 4 Absorbance for Surfaces with Random Roughness

The irregularity of surface (or interface) can be satisfactorily described by a statistically homogeneous random surface $\zeta(\vec{r}_{||})$. The statistics for such centered Gaussian fields (surfaces) may be written as the surface structure factor, $\langle |\hat{\zeta}(\vec{K}_{||})|^2 \rangle$, which is the Fourier transform of the surface correlation function [46, 49]. The surface structure factor or power-spectrum of roughness is the ensemble average of all the possible configurations. The ensemble averaged Fourier transformed surface profile and its correlation is assumed to follow the equation below

$$
\langle \hat{\zeta}(\vec{K}_{||}) \rangle = 0
$$

$$
\langle \hat{\zeta}(\vec{K}_{||}) \hat{\zeta}(\vec{K}'_{||}) \rangle = (2\pi)^2 \delta \left( \vec{K}_{||} + \vec{K}'_{||} \right) \langle |\hat{\zeta}(\vec{K}_{||})|^2 \rangle.
$$

To calculate the absorbance for a random electrode-electrolyte interface, we have to find the mean absorbance which senses the surface morphology through the single surface roughness characteristics, the surface structure factor [49]. The spectroelectrochemically observed quantity, the total absorbance for electrode-electrolyte interface in Laplace domain for the two dimensional homogeneous ran-
dom rough surface is given by

$$\langle A(p) \rangle = \epsilon C_0 \frac{q}{p(1 + \theta)} \left\{ 1 + \frac{q}{(2\pi)^2} \int d^2 K_\parallel [q_\parallel - q] \langle |\hat{\zeta}(K_\parallel)|^2 \rangle \right\}.$$  (4.0.2)

The inverse Laplace transform of it is written as:

$$\langle A(t) \rangle = \frac{2 \epsilon C_0 \sqrt{Dt}}{\sqrt{\pi}(1 + \theta)} \left( 1 + \hat{R} \langle |\hat{\zeta}(K_\parallel)|^2 \rangle \right),$$  (4.0.3)

where operator $\hat{R}$ bring in dynamic effect of surface roughness on the absorbance through its action on power-spectrum of roughness of electrode, given by

$$\hat{R} = \frac{1}{2(2\pi)^2 D t} \int d^2 K_\parallel K_\parallel^2 \left( 1 - \exp(-K_\parallel^2 D t) - \sqrt{\pi K_\parallel^2 D t} \text{erf} \left( \sqrt{K_\parallel^2 D t} \right) \right).$$  (4.0.4)

Equation 4.0.3 is an elegant equation for the ensembled averaged absorbance-transient in terms of surface structure factor. This equation possess information of various morphological features of the rough electrode surface (or interface) and, provides physical insights into anomalies and possible interpretation for the spectroelectrochemical response.

To correlate the average absorbance with the various morphological features of the surface, we consider first the short time behaviour of Eq. 4.0.3. Noting that the 2k-th moments of power-spectrum is related to mean square derivatives of surface profile [49], we have

$$m_{2k} = \frac{1}{(2\pi)^2} \int d^2 K_\parallel K_\parallel^{2k} \langle |\hat{\zeta}(K_\parallel)|^2 \rangle = \langle (\nabla_\parallel^k \zeta(r_\parallel))^2 \rangle.$$  (4.0.5)

Expansion of Eq. 4.0.3 for small $t$ results in equation which clearly interrelate absorbance to several morphological features of roughness. Equation of absorbance transient of electrogenerated species in term of moments of power-spectrum or
mean square derivatives of roughness is as follows:

\[
\langle A(t) \rangle = 2 \epsilon C_0^0 \sqrt{D t} \left(1 + \sum_{k=0}^{\infty} \frac{(-1)^k m_{2k+2}}{2(k+1)(2k+1)k!} (D t)^k \right) \tag{4.0.6}
\]

\[
= 2 \epsilon C_0^0 \sqrt{D t} \left(1 + \frac{1}{2} \langle (\nabla \| \zeta)^2 \rangle - \frac{1}{12} \langle (\nabla^3 \| \zeta)^2 \rangle D t + \cdots \right). \tag{4.0.7}
\]

Above equation may be recast in term of explicit physical features of roughness, viz, the excess surface area and mean square mean curvature \(\langle H^2 \rangle\) as:

\[
\langle A(t) \rangle = 2 \epsilon R C_0^0 \sqrt{\pi} (1 + \theta) \left(1 - \frac{\triangle A}{A_0} - \frac{(H^2)}{3} D t + \cdots \right), \tag{4.0.8}
\]

where the excess area is given by \(\triangle A/A_0 = \langle (\nabla \| \zeta)^2 \rangle /2\), the mean curvature given approximately by \(H \approx \frac{1}{2} \nabla^2 \| \zeta(r)\) and the ensemble averaged mean curvature for random surface is

\[
\langle H^2 \rangle \approx \frac{1}{4} \langle (\nabla^2 \| \zeta(r))^2 \rangle. \tag{4.0.9}
\]

Eq. 4.0.8 suggests that at very early times, the absorbance transient behaves as that of a smooth surface electrode (with excess area), and after some time it starts sensing local shape of the electrode and as time progresses it sees the contribution of higher and higher derivatives of the surface profile.

Next, we consider the long time asymptotic expansion of Eq. 4.0.3 which is obtained by using an asymptotic for \(- \text{erf}(\sqrt{K^2_{\|} D t}) \sim 1 - \exp(-K^2_{\|} D t)/\sqrt{\pi K^2_{\|} D t} [59]. We find,

\[
\langle A(t) \rangle = \frac{2 \epsilon R C_0^0 \sqrt{D t}}{\sqrt{\pi} (1 + \theta)} \left(1 - \frac{m_0}{2 D t} + \cdots \right). \tag{4.0.10}
\]

Thus, in the long time limit, the mean absorbance is sensitive to geometrical characteristics like the average roughness or mean square width of roughness, i.e. \(m_0 = h^2\). Equations 4.0.8 and 4.0.10 clearly demonstrate that absorbance-transients strongly depend on the morphological characteristics like mean square (MS) width, MS gradient, MS curvature, etc.
5 Absorbance Properties of Isotropic Self-Affine Fractal Surface

Fractal geometry is a very useful tool for describing many natural and artificial surface topography. Most of these surfaces are described in terms of idealized fractals for the sake of simplicity. Idealized fractal models take into account the roughness over an infinite length scales. However, these idealized fractal roughness profiles cannot be handled rigorously for practical purposes because of their peculiar mathematical properties, among which non-differentiability and non-stationarity restrict their applicability in physical systems. Therefore, for practical purposes and realistic modeling of roughness the band-limited self-affine fractal are often taken into consideration [53].

Fractal surfaces, which exhibit statistical self-resemblance over all length scales, can be described by the complete power law power-spectrum. However any real fractal surface is characterized by power law spectrum over few decades in wave-numbers with a high and a low wave-number cutoff. The band-limited power law spectrum in several cases shows a gradual flattening for low wave-number and a sharp decrease for the high wave-numbers. Such power spectrum can be estimated by a function with a sharp cutoff at low wave-numbers and a sharp cutoff at high wave-numbers (i.e. power at high wave-number is very small and low wave-numbers features does not contribute significantly to flux heterogeneity in diffusion controlled mass transfer) which is given by [52, 53].

\[
\langle |\hat{\zeta}(K_\parallel)|^2 \rangle = \mu |K_\parallel|^{2D_H-7}, \frac{1}{L} \leq |K_\parallel| \leq \frac{1}{l}.
\]  

(5.0.1)

From this statistical framework we get four fractal morphological characteristics of power-spectrum of roughness namely, fractal dimension \(D_H\), strength of fractality (\(\mu\)), lower and upper cut-off length scales (\(\ell\)) and (\(L\)). The fractal dimension \(D_H\) is the global property that describes the scale invariance property of the roughness and largely associated with anomalous behavior in diffusion controlled response, hence its time exponent is usually assumed to be function of roughness. The strength of fractality (\(\mu\)) is the measure of width of the interface and related
to topothesy. The geometrical interpretation of the topothesy as the length scale over which the profile has a mean slope of 1 \[54\]. The lower cut-off length scale (\(\ell\)) is the length above which we observe roughness and upper cut-off length scale (\(L\)) is the length above which we do not observe the roughness. As mentioned earlier, the moments of power spectrum of roughness have important morphological information. In general, \(m_{2k}\) are the \(2k\)-th moments of the power-spectrum of band-limited fractal and its expression is given as [47]:

\[
m_{2k} = \frac{\mu}{4\pi} \left( \frac{l^{-2(\delta+k)}}{\delta+k} - \frac{L^{-2(\delta+k)}}{\delta+k} \right).
\]  

(5.0.2)

These moments have physical significance as they are measures of morphological features of rough surface, viz, \(m_0\), \(m_2\) and \(m_4\) are mean square (MS) width, MS gradient and MS mean curvature of roughness, respectively.

The exact representation of absorbance for isotropic self-affine fractal surface is obtained by substituting Eq. 5.0.1 in Eq. 4.0.3 and representing various integrals in terms of special functions. The mean absorbance for realistic fractal roughness is as follows:

\[
\langle A(t) \rangle = A_P(t)(1 - R_{F1}(t) + R_{F2}(t, l) - R_{F2}(t, L))
\]

(5.0.3)

\[
R_{F1}(t) = \frac{m_0}{2Dt} + \left( \frac{\mu}{8\pi(Dt)^{D_H-3/2}} \right) \Gamma \left( D_H - \frac{5}{2}, \frac{Dt}{l^2}, \frac{Dt}{L^2} \right),
\]

\[
R_{F2}(t, \lambda) = \frac{\mu}{8\pi(D_H - 2)\lambda^{2D_H-3}} \sqrt{t^*} \left( \sqrt{\pi} \text{erf}(\sqrt{t^*}) - t^{*2-D_H} \gamma(D_H - \frac{3}{2}, t^*) \right),
\]

where dimensionless time \(t^* = \frac{Dt}{\lambda^2}\), \(\Gamma(\alpha, x_0, x_1) = \Gamma(\alpha, x_0) - \Gamma(\alpha, x_1) = \gamma(\alpha, x_1) - \gamma(\alpha, x_0)\), \(\Gamma(\alpha, x_i)\) and \(\gamma(\alpha, x_i)\) are the incomplete Gamma functions [50] and the minimum wave-number \((1/L)\) and maximum wave-number \((1/l)\) are two cutoff wave-numbers in power-spectrum.

An alternative method for derivation of leading asymptotic form of Eq. 5.0.3 is from leading asymptotic form of current transient equation of ref. [46, 47]. The approximate form of the current for an isotropic self-affine fractal surface can be
\[
\langle I(t) \rangle \approx \frac{nFDA_0C_0^0}{\sqrt{\pi D^t}(1 + \theta)} \left( 1 + \frac{\mu}{8\pi} \left( \frac{t^{-2\delta}}{\delta Dt} - \frac{\Gamma(\delta)}{(Dt)^{\delta + 1}} \right) \right), \quad t > t_i, \quad (5.0.4)
\]

where \( \delta = D_H - 5/2 \). Equation 5.0.4 is applicable for time greater that the inner fractal crossover time, \( t_i \). Integrating Eq. 5.0.4 between limits \( t_i \) and \( t \), we obtained asymptotic expression for charge-transient. Substituting charge transient in Eq. 1.0.1 we obtained expression for the absorbance transient. The absorbance for \( t \gg t_i \) for isotropic self-affine fractal electrode-electrolyte interface is given by

\[
\langle A(t) \rangle \approx \frac{2\epsilon C_0^0 \sqrt{Dt}}{\sqrt{\pi(1 + \theta)}} \left( 1 - \frac{\mu}{8\pi \delta Dt} + \frac{\mu \Gamma(\delta)}{8\pi(2\delta + 1)(Dt)^{\delta + 1}} \right), \quad t \gg t_i. \quad (5.0.5)
\]

The inner fractal crossover time, \( t_i \), is the time after which anomalous intermediate time regime is observed in the current or absorbance. Contribution of \( \langle A(t_i) \rangle \) is small for all \( t \gg t_i \), hence it is ignored in above formula.

The inner crossover time, \( t_i \), is the time after which anomalous intermediate time regime is observed in the absorbance and is used to mark the scaling region of the absorbance. Equating Eq. 4.0.8 and Eq. 5.0.5, we obtain for \( t_i \)

\[
\frac{m_2}{2} - \frac{m_4 Dt_i}{12} = \frac{\mu \Gamma(\delta)}{8\pi(2\delta + 1)(Dt_i)^{\delta + 1}} - \frac{\mu \ell^{-2\delta}}{8\pi \delta Dt_i}. \quad (5.0.6)
\]

\( t_i \) is obtained by the solution the above equation, and the region near \( t_i \) can be observed if the observation time window starts at a time smaller than \( t_i \). The inner transition is a strong function of fractal dimension and lower cutoff length (\( \ell \)) through \( m_2 \approx (\mu/4\pi) \left[ \ell^{-2(\delta + 1)/\delta + 1} \right] \) and \( m_4 \approx (\mu/4\pi) \left[ \ell^{-2(\delta + 1)/(\delta + 2)} \right] \). Similarly, the outer transition time, \( t_o \), is the time at which anomalous time behavior of the absorbance ends. The time \( t_o \) cannot be obtained by equating Eq. 4.0.10 and Eq. 5.0.5, as the intermediate and long time asymptotically merge with each other at very long times. Outer crossover time \( (t_o) \) can be estimated using method discussed in ref. 50.
6  Absorbance for Nonfractal Electrode Surfaces

In most of the cases electrode roughness is modeled as realistic fractals but in some cases, roughness clearly has no self-similarity property and has a dominant length scale of randomness. Such roughness can be modeled with a power-spectrum function with a single lateral correlation length. One of the statistical models for non-fractal surfaces can be described in terms of a Gaussian correlation function \( W(\vec{r}) \) with a mean MS width \( h^2 \) and a correlation length, \( a \). The Gaussian correlation function is given as [49, 55]:

\[
W(\vec{r}) = h^2 e^{-r^2/a^2}.
\]  

(6.0.1)

Its Fourier transform is the surface structure factor which possesses various morphological features for the non-fractal surfaces, and is given by

\[
\langle |\hat{\zeta}(\vec{K})|^2 \rangle = \pi h^2 a^2 e^{-K_i^2 a^2/4}.
\]  

(6.0.2)

In this framework, we get two morphological parameters viz, width of the interface, \( h^2 \), and transversal correlation length, \( a \). The transverse correlation length \( (a) \) is the length which is a measure of the average distance between consecutive peaks and valleys on the random non-fractal surface and \( h \) is the measure of mean square departure of the surface from flatness. The excess surface area, \( A_{\text{real}} \) and average square gradient are related as

\[
\frac{1}{2} \langle (\nabla_i \zeta)^2 \rangle = \frac{A_{\text{real}}}{A_0} = R^* - 1 = \frac{2h^2}{a^2},
\]

where \( A_0 \) is the projected area of the electrode and \( R^* \) is the roughness factor which is given by \( R^* = 1 + 2(h/a)^2 \). The ensemble averaged mean square curvature is

\[
\langle H^2 \rangle \approx \frac{8h^2}{a^4}.
\]

The ensemble averaged absorbance \( \langle A(t) \rangle \), for non-fractal electrode surface (or interface) is given by

\[
\langle A(t) \rangle = \frac{2\epsilon_R C_O^0 \sqrt{D t}}{\sqrt{\pi}(1 + \theta)} \left( 1 + \frac{h^2 \tan^{-1}\left( \frac{2\sqrt{D t}}{a} \right)}{a \sqrt{D t}} \right).
\]  

(6.0.3)

The second term in the parentheses in the above equation, is the contribution due
to roughness. If the roughness \( h^2 \) is zero then only first term survives giving smooth electrode response. Equation 6.0.3 for absorbance is related to current transient in ref. [49, 50] through an integration with respect to time of the mean current for a Gaussian power-spectrum of roughness.

7 Results and Discussion

In this section we will analyse absorbance transients in details for realistic self-affine fractal electrodes as well as for non-fractal electrodes. Figure 2.1 depicts the rough OTE with fractal morphological and phenomenological scales which control the spectroelectrochemical response. As discussed earlier, the power-spectrum of such roughness consists of four morphological characteristics, viz, the fractal dimension \( D_H \), lower \( l \) and upper \( L \) cutoff length scales of fractality and a proportionality factor \( \mu \) or strength of fractality. Out of four only three, i.e. \( D_H \), \( \mu \) and \( l \), contribute strongly to the electrochemical response of electrode while \( L \) contributes weakly.

Figures 2.2, 2.3 and 2.4 are the log-log plot of absorbance and time which illustrates the change in absorbance with time while varying one of the dominant morphological parameters, i.e. \( D_H \), \( \mu \) and \( l \), respectively. These figures illustrate existence of three time regimes, that is, short, anomalous intermediate and long time regimes. The anomalous intermediate and long time regimes are seen in the plot. The short time regime with square root time dependence has not been visible in the plots because it does not come in the time region shown in the figure.

The anomalous intermediate regime for the absorbance can also be characterized by using scaling arguments. The de Gennes scaling law for the diffusion controlled current is given as [56, 57, 58]: \( I \propto t^{-\beta} \) and its time integration is proportional to the total charge used in reaction or absorbance. The scaling form of absorbance transient is as follows:

\[
A(t) \propto t^{-\beta+1}
\]  

(7.0.1)

where the exponent, \( \beta \), depends on interfacial roughness given by \( \beta = \frac{D_H - 1}{2} \) and
It varies from 0.5 (planar surface) to 1 thus, $D_H$ varies from 2 (planar surface) to 3 (nearly porous surface), respectively. From this, for $D_H = 2$ scaling exponent in absorbance becomes 0.5 while $D_H = 3$ it is 0. This means, if fractal dimension approaches 3 absorbance is very weakly dependent on time and the intermediate region becomes flatter. In other words, if roughness increases initially absorbance also increases and after a certain value the absorbance shows a weak dependence on time in the intermediate region (see Figures 2.2, 2.3 and 2.4) and shows smooth electrode response in the long time regime. It is clear that the scaling result in Eq. 7.0.1 is unable to include a complete set of realistic fractal morphological characteristics of roughness and because of this reason it cannot capture all aspects of experimental data. Particularly, difficulties arise in the transition region and often mix the data of the scaling region with the transition region, and hence there is an inaccurate prediction of fractal dimension with scaling relations.

Fig. 2.2 demonstrates the variation of absorbance transient with fractal dimension. As the fractal dimension increases roughness factor also increases, magnitude of absorbance transient increases but after the certain value fractal dimension the anomalous intermediate region show weak dependence on time. Fig. 2.3 illustrates the variation of absorbance with width of the interface. If width of the interface increases roughness factor also increases. The absorbance transient increases but after the certain value of roughness, the anomalous region becomes flat or approximately time independent. Similarly, if lower cutoff length scale decreases roughness factor also increases. Again absorbance increases in the initial time but anomalous region starts becoming flatter with increase in roughness due to lowering of lower cutoff length. Therefore, there is a similar kind of observation either we increase the width of the interface (or strength of fractality) in Fig. 2.3 or decrease the lower cut-off length scale in Fig. 2.4 as in case of increase of fractal dimension in Fig. 2.2. Inset figures depict traditional representation of absorbance transient where abscissa is $\sqrt{t}$ and ordinate is $A$. These figures depict smooth surface response as a straight line while rough electrode enhanced response with curved lines. Traditional representation does not explicitly reveal various time regimes.

From the above discussion it is clear that absorbance is not only strongly de-
dependent on fractal dimension but also on other two morphological parameters, $\mu$ and $\ell$. Thus, rigorous theory based on power spectrum of roughness character-
izes three regimes, viz, an anomalous intermediate region along with short and long time regimes more efficiently and accurately than one based on the scaling approach. The double logarithmic plots of the absorbance and time give more insights into the physical picture in all regimes and explain the transition times as well which is not possible to observe in non logarithmic traditional plots $A(t)$ vs $\sqrt{t}$ (see inset plots). As expected, it is linear for smooth electrode surface (first plot from bottom). As the roughness increases it increases absorbance and absorbance starts to deviate from linear response because of roughness contributions. The deviation is larger with the change in morphological features which increase the roughness factor especially in the short time and enhancing the absorbance as well.

Figure 2.5 shows the absorbance transients of non-fractal rough electrode and illustrate the effect of two non-fractal morphological characteristics, viz, MS width ($h^2$) and transversal correlation length ($a$). Figures are plotted as double log plot of absorbance vs time while traditional plots $A(t)$ vs $\sqrt{t}$ are shown in inset. Common observations in this case are the presence of three time regions, that are, short time $\sqrt{t}$ region, intermediate transition region and long time $\sqrt{t}$ region. Here the short time regime fall within experimental time scales in the plots. Fig. 2.5 show that if width of the interface increases absorbance also increases and outer crossover time ($t_o$) also increases. In the short time regime absorbance transient increases by a roughness factor while follows $\sqrt{t}$ behavior, in the intermediate transition regime there is slow decrease in slope of double log plots of the absorbance transient and eventually becomes weakly dependent of time at higher value of roughness factor. Finally, it merges with the planar response in the long time regime. Fig. 2.6 show that if we decrease the transverse correlation length, $a$, the roughness factor as well as absorbance increases. Thus, in the short time regime absorbance transient increases by a roughness factor while in the intermediate regime of absorbance increases but show weaker dependence, these effects are very similar to one sees in fractal OTE. Long time regime all responses merge with the smooth surface absorbance.
Figure 2.2: Effect of fractal dimension on absorbance-transients. The above curves are generated by using: $D_H = 2.00, 2.15, 2.20, 2.25,$ and $2.30$ (from bottom), $\ell = 50\, \text{nm}$, $L = 10^3\, \text{nm}$ and $\mu = 10^{-5}$ (a.u.). Other parameters used in the calculations are as: Diffusion coefficient ($D = 5 \times 10^{-6}\, \text{cm}^2/\text{s}$), concentration ($C_0 = 10^{-6}\, \text{mol/cm}^3$), and $\epsilon = 10^5\, \text{cm}^2/\text{mol}$.
Figure 2.3: Effect of strength of fractality on absorbance-transients. The above curves are generated by using: $\mu = \mu_0$, $5 \times \mu_0$, $10 \times \mu_0$, and $20 \times \mu_0$ (a.u.) (from bottom) where, $\mu_0 = 10^{-6}$, $D_H = 2.25$, $\ell = 50$ nm and $L = 10^3$ nm. Other parameters used in the calculations are as: Diffusion coefficient ($D = 5 \times 10^{-6}$ cm$^2$/s), concentration ($C_0 = 10^{-6}$ mol/cm$^3$), and $\epsilon = 10^5$ cm$^2$/mol.
Figure 2.4: Effect of lower cut-off length scale on absorbance-transients. The above curves are generated by using: $\ell = 50, 100, 200, \text{ and } 400 \, \text{nm}$ (from top), $D_H = 2.25, \mu = 10^{-5}(\text{a.u.})$ and $L = 10^3 \, \text{nm}$. Other parameters used in the calculations are as: Diffusion coefficient ($D = 5 \times 10^{-6} \, \text{cm}^2/\text{s}$), concentration ($C_0 = 10^{-6} \, \text{mol/cm}^3$), and $\epsilon = 10^5 \, \text{cm}^2/\text{mol}$.
Figure 2.5: Effect of width of the interface, \( h \), at fixed correlation length on absorbance-transient for nonfractal OTE. The plots are generated by using: \( h = 3, 5, 7, 10 \, \mu m \) (from bottom), and \( a = 6 \, \mu m \). Other parameters are used in the above calculations are as: Diffusion coefficient \((D = 5 \times 10^{-6} \, cm^2/s)\), molar absorptivity \((\epsilon = 10^5 \, cm^2/mol)\), concentration \((C_0^0 = 10^{-6} \, mol/cm^3)\).
Figure 2.6: Effect of transversal correlation length, $a$, at fixed rms width of the interface on absorbance-transient for nonfractal OTE. The plots are generated by using: $a = 1, 2, 4, 8 \, \mu m$ (from top), and $h = 5 \, \mu m$. Other parameters are used in the above calculations are as: Diffusion coefficient ($D = 5 \times 10^{-6} \, cm^2/s$), molar absorptivity ($\epsilon = 10^5 \, cm^2/mol$), concentration ($C_0 = 10^{-6} \, mol/cm^3$).
8 Conclusions

The theory developed in present paper enables us to discern the effect of morphology of electrodes on diffusion controlled reactions and their influence on chronoabsorptometric and chronocoulometric measurements. The theory developed here allows us to address deterministic as well as stochastic surface roughness in OTE. Stochastic morphology offers realistic models of roughness which may have fractal or non-fractal nature. The randomly rough surface can be characterized by using a power spectrum of roughness. The conclusions drawn are: (1) absorbance increases with increase in roughness of surface, (2) at very early times diffusion layer thickness is small compared to roughness features, the electrode response is similar to a planar electrode (with excess area), after a certain time it starts to sense the local shape of the electrode and as time progresses it senses the contribution of higher and higher derivatives of the surface, (3) the intermediate regime shows anomalous power-law behaviour but at higher value of roughness factor it becomes weakly dependent on time and finally for large roughness it is independent of time, (3) scaling law for absorbance of fractal OTE based on de Gennes scaling expression for the flux does capture some features of intermediate times but it is not sufficient for the characterization of all regions in absorbance transients, (4) long time regime occurs when diffusion layer thickness is larger than the mean square width of interface and (5) our ab initio methodology based on the power spectrum of roughness characterizes all the three regions in absorbance successfully. Our theoretical model successfully provides the physical picture which relates response to phenomenological length- the diffusion length, and morphological length scales which characterizes the nature of the rough surface. These findings provide insights for spectroelectrochemical responses and techniques which can be critical for assigning the mechanisms, identification of intermediates, products and other electron transfer processes taking place at an electrode-electrolyte interface. Finally one can say, this theory is an indispensable step in the quantitative description of the role of roughness on single potential step chronoabsorptometric response of an optically transparent electrode.
9 Appendix : Transition times

The double logarithmic plot of absorbance and time has three distinct time regions. The short time region, when the diffusion layer thickness is small as compared to the surface irregularities. The intermediate time region, when the diffusion layer thickness is comparable to the surface irregularities. Finally, the long time region, when the diffusion layer thickness is much larger than the surface irregularities. Thus, the intermediate time region is the region of transition from short time asymptotic to long time asymptotic behavior. The inner fractal crossover time, \( t_i \), is the time after which anomalous intermediate time regime is observed in the absorbance and is used to mark the scaling region of the absorbance \([46, 50]\). This is obtained by the solution of the following equation:

\[
\frac{m_2}{2} - \frac{m_4 D t_i}{12} = \frac{\mu \Gamma(\delta)}{8 \pi (2\delta + 1)(D t_i)^{\delta + 1}} - \frac{\mu \ell^{-2\delta}}{8 \pi \delta D t_i} \tag{9.0.1}
\]

Similarly, the outer transition time, \( t_o \), is the time at which anomalous time behavior of the absorbance ends. This cannot be like inner crossover time as the intermediate and long time asymptotically merges with each other instead of crossing at a common point and hence one obtain overestimate for the value of \( t_o \) \([46]\). This can be estimated analogous to ref. \([50]\) as:

\[
\frac{\mathcal{A}_R(t_o) - 1 + m_0/(2 D t_o)}{\mathcal{A}_R(t_o)} = 0.1 \tag{9.0.2}
\]

where \( \mathcal{A}_R(t_o) = \langle A(t_o) \rangle / A_P(t_o) \) is the relative absorbance and is obtained by taking the ratio of the Eq. 5.0.5 to the planar response that is, \( \mathcal{A}_R(t_o) = 1 + \frac{\mu \Gamma(\delta)}{8 \pi (2\delta + 1)(D t_o)^{\delta + 1}} - \frac{\mu \ell^{-2\delta}}{8 \pi \delta D t_o} \). This means that, the deviation for the outer transition time between the intermediate and planar response is around 10 percent, Eq. 9.0.1.
Bibliography


