Chapter 3

Theory of Chronoabsorptometry of a Pseudo First-order Catalytic Process at an Optically Transparent Rough Electrode
Abstract

A theoretical model for absorbance-transient has been developed for the pseudo first-order catalytic coupled reaction (EC') mechanism at rough optically transparent electrode (OTE). A second-order perturbation solution in surface profile for an arbitrary rough surface is obtained. Results are obtained for the realistic surface roughness model. The realistic surface roughness can be fractal, nonfractal or combination of these two geometries which is characterized by using the power-spectrum of roughness. We obtained the expression for the absorbance-transient at the rough OTE surface for band limited self-affine fractal roughness. An extension of the Danckwerts’ expression in terms of the absorbance at rough OTE-electrolyte interface is also obtained. Our results show an enhancement in the absorbance-transients due to the roughness present at the OTE surface. The double logarithmic plot of absorbance-time gives the two time regimes, i.e. anomalous intermediate and long-time regimes. The anomalous intermediate-time regime gives the information related to the surface morphology. This regime shows strong dependency on the fractal morphological characteristics while the long-time regime is the time dependent kinetic-controlled regime.
1 Introduction

The term “catalytic” electrochemical response is applicable to all types of electrochemical responses in which the product being consumed in the electrochemical reaction is partially regenerated by some chemical process involving a product of the electrochemical reaction [1]. If the species is photoactive and interacts with the appropriate range of electromagnetic radiation then, spectroscopic study can also be done simultaneously. The surface morphology or geometry of an electrode (where the photoactive species is generated) affects the spectroelectrochemical responses (current, charge and absorbance) significantly. It is almost inevitable to produce an electrode surface which is perfectly smooth especially, electrodes made of solid metals (Pt, Au, Ru, etc.), doped oxide semi-conductors (SnO$_2$, InO$_2$, etc.), films, etc. It was reported by several authors [2, 3, 4] that absorbance-transient may be affected by electrode surface roughness during spectroelectrochemistry measurements. Especially, by Richard L. McCreery and co-workers [3] who pointed out that Absorbance vs time$^{1/2}$ plot for the minigrid electrodes show deviation from linearity in the short time (below 50 ms) may be due to the electrode surface roughness.

The rough electrodes have potential to enhance the surface reactions upto many folds. This kind of surface morphology is useful in fundamental to applied fields [5, 6, 7, 8, 9, 10] which is well known these days. Due to the complexity for the characterization of the rough surface, this problem is still not well understood which has significance in the spectroelectrochemical measurements. Hence, understanding the influence of morphology or roughness of an optically transparent electrode on the catalytic coupled reaction systems is of utmost importance [5].

The pseudo first-order catalytic coupled reaction mechanism (EC’) was first characterized using spectroelectrochemistry by Winograd et. al [11] in 1969, assuming that the surface of the OTE is smooth. The scheme for EC’ reaction is represented as: $O + ne^- \rightarrow R + z \xrightarrow{k} O + z'$ where $k$ is homogeneous rate constant, $z$ and $z'$ are electrochemically inactive at the electrode potential at which reaction proceed [1]. The spectroelectrochemical studies of catalytic coupled reaction mechanism is one of the most important class of reactions which is
Figure 3.1: Schematic diagram of pseudo first-order catalytic coupled reaction (EC’) mechanism process, $O + ne^- \rightleftharpoons R + z \xrightarrow{k} O + z'$ at fractally rough OTE-electrolyte interface. The various morphological and phenomenological characteristics that control the absorbance-transients for the EC’ reaction mechanism are as: fractal dimension ($D_H$), lower cut-off length scale ($\ell$), upper cut-off length scale ($L$), width of the interface ($h$), diffusion width ($\sqrt{Dt}$) and homogeneous rate constant ($k$). Here $z$ is catalyst and electrochemically inactive at the potential where this reaction takes place.
used in the study of fuel cells [1, 12], biomolecules [13, 14, 15, 16, 17], organo-
metallic catalysis [18, 19], electrosynthetic reactions [18, 20, 21], secondary bat-
tery system and studies of metallic corrosion [12] and in other applied fields
[13, 14, 15, 16, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39].
Therefore, it is of great interest to examine the kinetic behavior of the catalytic
coupled reaction mechanism at modified or rough OTEs to gain further insight
into the surface influence in the mechanism of catalytic reactions.

The use of the catalytic coupled reaction mechanisms to measure homogeneous
electron transfer rates of reactions has greatly expanded the opportunities to ap-
ply electrochemistry to problems in other areas of chemistry [11, 16, 17, 40, 41].
J. H. Christie [42] calculated the total charge for the pseudo first-order catalytic
coupled reaction at smooth electrode in 1967. The chronoabsorptometry resem-
bles chronocoulometry [43] but chronoabsorptometry has several advantages over
chronocoulometry [11]. J. H. Christie [42] had derived the expression of the charge-
transient for pseudo first-order catalytic coupled reaction. After this, Winograd
et al. [11, 17] derived and experimentally verified the total absorbance-transient
response at smooth OTE for pseudo first-order catalytic coupled reaction scheme
which can be written as:

$$A_C(E, t) = A_P(t) \left\{ \frac{2 \sqrt{k t} e^{-kt} + \sqrt{\pi} (1 + 2 k t) \text{erf}(\sqrt{k t})}{4 \sqrt{k t}} \right\}, \quad (1.0.1)$$

where $A_C(E, t)$ is the total absorbance for EC’ reaction mechanism at smooth
OTE which is function of potential ($E$) and time ($t$), $k$ is homogeneous rate
constant, “erf” is the error function [44] and $A_P(t)$ is the absorbance-transient
for the diffusion-limited process at the planar OTE without any catalytic coupled
reaction, given as [43]:

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

where $\epsilon$ is the molar absorptivity, $C^0_O$ is the bulk concentration of the oxidized
species and $D$ is the diffusion co-efficient.

The rate of the heterogeneous regenerative process is strongly dependent upon
the nature of the electrode material and the state of its surface. The roughness
present at the OTE surface can show fractal, nonfractal or combination of these two geometries. It is reported by Vladimir M. Shalaev et al. [45, 46] and Markel et al. [47] that, due to the fractal nature of the rough surface, the absorbance is localized in “hot zones” and “cold zones” which causes large enhancement in the absorbance as compared to nonfractal or smooth surface. It has also been reported that, the rough electrodes provide better alternatives to enhance the surface reactions for many fundamental and applied applications [5, 6, 7, 8, 9, 10]. Therefore, the EC’ reaction mechanism at rough OTE surface can be used to enhance the performance of the fuel cell devices, photovoltaics, solar cells, OLED, electrochromic devices, etc. In the present chapter, we analyze the effect of the OTE surface roughness on the generation of the photoactive species and its subsequent effects on the absorbance-transient response for EC’ reaction mechanism.

The present chapter is organized as follows: the first section deals about the formulation of the problem and in the second section we present the second-order perturbation solution for an arbitrary rough surface profile. Random roughness of an OTE surface is dealt in the third section followed by band limited self-affine nature of the rough OTE in the fourth section. Finally, results are discussed and conclusions are drawn.

2 Formulation

The pseudo first-order catalytic coupled reaction scheme is represented as: \( O + ne^- \rightarrow R+z \xrightarrow{k} O+z' \). If the species is photoactive then the change in absorbance can be determined, if we know the concentration profile of that photoactive species. This concentration profile \( C_i(\vec{r}, t) \) around the rough electrode is determined by solving the appropriate diffusion equation. For an EC’ reaction the concentration profile satisfies the diffusion equation as:

\[
\frac{\partial}{\partial t} \delta C_i(\vec{r}, t) = D_i \nabla^2 \delta C_i(\vec{r}, t) - k \delta C_i(\vec{r}, t),
\]

where \( k \) is the first-order homogeneous rate constant, \( i \equiv O, R \) represents the oxidized or reduced species respectively, \( \delta C_i(\zeta) \) 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, $\vec{r} \equiv (x, y, z)$. In our calculation we assume that, $\delta C(\vec{r}, t) = \delta C_0(\vec{r}, t) = -\delta C_R(\vec{r}, t)$. Thus,

$$\frac{\partial}{\partial t} \delta C(\vec{r}, t) = D \nabla^2 \delta C(\vec{r}, t) - k \delta C(\vec{r}, t). \quad (2.0.2)$$

For purely diffusion-controlled reversible redox reaction, i.e. when $k = 0$, the above equation (Eq. 2.0.2) is reduced as:

$$\frac{\partial}{\partial t} C_i(\vec{r}, t) = D_i \nabla^2 \delta C_i(\vec{r}, t). \quad (2.0.3)$$

Equation 2.0.2 can be transformed to simple diffusion equation by using the transformation

$$\delta C^* = e^{kt} \delta C$$

$$\frac{\partial}{\partial t} \delta C^*(\vec{r}, t) = D \nabla^2 \delta C^*(\vec{r}, t). \quad (2.0.4)$$

To complete the transformation of the boundary value problem to a simpler problem we need to transform the initial and the bulk boundary problems too. This is given by

$$\delta C^*(\vec{r}, t = 0) = 0$$
$$\delta C^*(\vec{r}_{||}, z \to \infty, t) = 0. \quad (2.0.5)$$

The surface boundary condition for both the processes (cathodic or anodic) are same. So, the transformed boundary condition is

$$\delta C^*(\vec{r}_{||}, t) = -e^{kt} C_S = -\frac{e^{kt} C^0_O}{1 + \theta}, \quad (2.0.6)$$

where $\theta = \exp(-nf(E_i - E^{0'}))$, $E_i$ and $E^{0'}$ are the initial and formal potentials respectively, $f = F/RT$, $F$ is Faraday constant, $R$ is gas constant, $T$ is absolute temperature, $C^0_O$ is the bulk concentration of the oxidized species and $n$ is number
of electrons involved in the redox reaction.

The local absorbance density, $\alpha(t)$, for the coupled catalytic (EC') reaction up to time ‘t’ is given by

$$\alpha(z = \zeta(r_\parallel), t) = \frac{\epsilon D}{A_0} \int_0^t \partial_n \delta C_O(z = \zeta(r_\parallel), t') \, dt',$$

(2.0.7)

where $\epsilon$ is the molar absorptivity and $A_0$ is the electrode geometric area. Therefore, the total absorbance over surface $\zeta(r_\parallel)$ at the interface up to time ‘t’ is given by

$$A(t) = \frac{\epsilon D}{A_0} \int_0^t \int_{S_0} dS_0 \beta \partial_n \delta C_O(z = \zeta(r_\parallel), t') \, dt'$$

$$= \int_{S_0} dx \, dy \beta \alpha(z = \zeta(r_\parallel), t),$$

(2.0.8)

where $\hat{n} = (1/\beta)(-\nabla_\parallel \zeta(r_\parallel), 1)$, $\nabla_\parallel = (\partial/\partial x, \partial/\partial y)$ and $\partial_n = \hat{n} \cdot \nabla$ signifies the outward drawn normal derivative at the surface. From above equation Eq. 2.0.8, it is clear that, to calculate the absorbance-transient at an electrode-electrolyte interface one need to evaluate the concentration profile around an arbitrary rough electrode-electrolyte interface.

3 Perturbative Solution for an Arbitrary Rough Surface Profile

The second-order perturbation solution for the concentration profile for weakly fluctuating two-dimensional rough surface in Fourier and Laplace transform domains is written as [48, 49]:

$$\delta C(K_\parallel, z, p) = \left( -\frac{C_0}{p} \right) e^{-\hat{q} \parallel \zeta} \left\{ (2\pi)^2 \delta(K_\parallel) + q_k \hat{\zeta}(\vec{K}_\parallel) \right.$$

$$\left. + \frac{q_k^2}{2(2\pi)^2} \int d^2 K_\parallel' \hat{\zeta}(\vec{K}_\parallel - \vec{K}_\parallel') \hat{\zeta}(\vec{K}_\parallel')[2\hat{\zeta}_\parallel(\parallel' - 1)] \right\} + O(\hat{\zeta}^3),$$

(3.0.1)
where $\hat{\zeta}(\vec{K}_\parallel)$ is the two dimensional Fourier transform of the rough surface profile $\zeta(\vec{r}_\parallel)$ and $\delta(\vec{K}_\parallel)$ is Dirac delta function in wave-number $\vec{K}_\parallel$ (or spatial frequency components in roughness). Other symbols in the above equation are defined as:

\[
q = \left(\frac{p}{D}\right)^{1/2}
q_k = \left[q^2 + k/D\right]^{1/2}
\tilde{q}_\parallel = q_k \gamma_\parallel = \left[q_k^2 + \vec{K}_\parallel^2\right]^{1/2}
\tilde{q}_{\parallel,\parallel'} = q_k \gamma_{\parallel,\parallel'} = \left[q_k^2 + (\vec{K}_\parallel - \vec{K}_{\parallel'})^2\right]^{1/2},
\]

where $k$ is homogeneous rate constant, $K_\parallel = |\vec{K}_\parallel|$, and $p$ is Laplace transform variable.

The perturbative solution for the local absorbance density, $\alpha(t)$, in Laplace and Fourier transformed domain for weakly and gently fluctuating two-dimensional rough surface is given as:

\[
\alpha(\hat{\zeta}, p) = \left(\frac{\epsilon}{A_0}\right) \left[ \hat{O}_0 (2\pi)^2 \delta(K_\parallel^2) + \hat{O}_1 \hat{\zeta}(K_\parallel) + \hat{O}_2 \hat{\zeta}(K_\parallel) \hat{\zeta}(K_\parallel - K_\parallel') \right],
\]

where $\hat{O}_0, \hat{O}_1, \hat{O}_2'$ are operators which are defined as:

\[
\hat{O}_0 \equiv \frac{q_k}{p^2}; \quad \hat{O}_1 \equiv \hat{O}_0(\tilde{q}_\parallel - q_k)
\hat{O}_2' \equiv \frac{1}{(2\pi)^2 p} \int d^2K_{\parallel'} \left[ \tilde{q}_{\parallel,\parallel'} - \frac{1}{2} (q_k^2 + q_k \tilde{q}_\parallel) - (K_\parallel - K_{\parallel'})^2 \right.
\left. - \frac{1}{2} \vec{K}_{\parallel'} \cdot (\vec{K}_\parallel - \vec{K}_{\parallel'}) \right].
\]

Therefore, the total absorbance in the Laplace transform domain at an arbitrary profile electrode surface is obtained by taking the surface integral of the absorbance density Eq. 3.0.3 and is given by

\[
\mathcal{A}(p) = \left(\frac{\epsilon}{A_0}\right) \int_{\mathcal{S}_0} d^2r_{\parallel} \left\{ \left[ \hat{O}_0 (2\pi)^2 \delta(K_\parallel^2) + \hat{O}_1 \hat{\zeta}(K_\parallel) + \hat{O}_2 \hat{\zeta}(K_\parallel) \hat{\zeta}(K_\parallel - K_\parallel') \right] ; \quad K_\parallel \rightarrow r_{\parallel}' \right\},
\]
where \(\hat{O}_2 \equiv \frac{1}{(2\pi)^p} \int dK' \left[ \tilde{q}_\parallel \tilde{q}'_\parallel - \frac{1}{2} (q_\parallel^2 + q_\parallel \tilde{q}_\parallel) - (\tilde{K}_\parallel - \tilde{K}'_\parallel)^2 - \tilde{K}_\parallel \cdot (\tilde{K}_\parallel - \tilde{K}'_\parallel) \right]\) which differ from \(\hat{O}_2'\) only in co-efficient of the last term and the operator \(\hat{O}_0\) and \(\hat{O}_1\) are same as in Eq. 3.0.4. \(\hat{O}_0, \hat{O}_1\) and \(\hat{O}_2\) are the operators for the smooth surface, the first and second-order terms in Laplace transformed domain, respectively. Equation 3.0.5 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 OTE Surface with Random Roughness

The morphological irregularity of surface (or interface) can be satisfactorily described as centered Gaussian fields which is statistically homogeneous random surface \(\zeta(\vec{r}_\parallel)\), where \(\vec{r}_\parallel\) is a two dimensional space vector. To understand the statistics for such Gaussian fields (surfaces), the surface structure factor, \(\langle |\hat{\zeta}(\vec{K}_\parallel)|^2 \rangle\), which is the Fourier-transform of the surface correlation function [48, 50], may be used. Here \(\langle \cdot \rangle\) represents the ensemble average. Thus, the surface structure factor or power-spectrum of roughness is the ensemble average over all the possible configurations. The equation which governs this ensemble averaged Fourier transformed surface profile and its correlation is given as:

\[
\langle \hat{\zeta}(\vec{K}_\parallel) \rangle = 0
\]

\[
\langle \hat{\zeta}(\vec{K}_\parallel) \hat{\zeta}(\vec{K}'_\parallel) \rangle = (2\pi)^2 \delta \left( \vec{K}_\parallel + \vec{K}'_\parallel \right) \langle |\hat{\zeta}(\vec{K}_\parallel)|^2 \rangle .
\] (4.0.1)

The mean electrochemical response for such random surface (or interface) can be given in terms of surface structure factor which senses the surface morphology [48]. The spectroelectrochemically observed quantity in UV-Visible range, i.e. the total absorbance for the two dimensional homogeneous random rough surface in...
Laplace domain is given as:

\[
\langle A(p) \rangle = \epsilon C_0 \frac{D q_k}{p^2 (1 + \theta)} \left\{ 1 + \frac{q_k}{(2\pi)^2} \int d^2 K || \hat{\tau} || \langle \hat{\xi}(K^2) \rangle \right\}. 
\] (4.0.2)

Above equation can be written in term of the Laplace transformed generalized Cottrell current \([48, 51]\) \((\langle I_{gc}(p) \rangle)\) for the rough electrode as:

\[
\langle A(p) \rangle = \epsilon n F A_0 \frac{D}{p(1 + \theta)} \left\{ 1 + \frac{q}{(2\pi)^2} \int d^2 K || \hat{\tau} || \langle \hat{\xi}(K^2) \rangle \right\}. 
\] (4.0.3)

\[
\langle I_{gc}(p) \rangle = n F A_0 \frac{D C_0}{q(1 + \theta)} \left\{ 1 + \frac{q}{(2\pi)^2} \int d^2 K || \hat{\tau} || \langle \hat{\xi}(K^2) \rangle \right\}. 
\] (4.0.4)

The inverse Laplace transform of Eq. 4.0.3 for pseudo first-order catalytic reaction mechanism can be rearranged as:

\[
\langle A(t) \rangle = \frac{\epsilon}{n F A_0} \int_0^t dt \left\{ 1 + k \int_0^t dt \right\} e^{-kt} \langle I_{gc}(t) \rangle 
\]

\[
= \int_0^t dt \left\{ 1 + k \int_0^t dt \right\} e^{-kt} \frac{d}{dt} \langle A_{ga}(t) \rangle 
\]

\[
= \left\{ 1 + k \int_0^t dt \right\}^2 e^{-kt} \langle A_{ga}(t) \rangle, 
\] (4.0.5)

where \(A_{ga}\) is the generalized absorbance for simple reversible redox reaction for purely diffusion-limited case that is, without kinetics.

Equation 4.0.5 represents the extension of the Danckwerts’ expression \([52]\) in terms of the absorbance on the rough OTE-electrolyte interface. This expression relates the absorbance-transients and the kinetics of the coupled (EC’) homogeneous reaction at the rough OTE-electrolyte interface \([5]\) as:

\[
\langle A(t) \rangle = e^{-kt} \langle A_{ga}(t) \rangle + 2k \int_0^t dt' e^{-kt'} \langle A_{ga}(t') \rangle + k^2 \int_0^t dt' \int_0^{t'} dt'' e^{-kt''} \langle A_{ga}(t'') \rangle. 
\] (4.0.6)

In the above Eq. 4.0.6, \(\langle A(t) \rangle\) and \(\langle A_{ga}(t) \rangle\) are the total absorbance for the
pseudo first-order catalytic (EC’) reaction mechanism and the absorbance for the purely diffusion-limited simple reversible redox reaction at rough OTE, respectively. The second term in the curly bracket in Eq. 4.0.5 introduces the kinetic effect of the pseudo first-order catalytic coupled reaction mechanism. The Eq. 4.0.6 is the extension of the Danckwerts’ expression [52] in terms of the absorbance which is the first of its kind. Since, the simplest Danckwerts’ expression for current requires a linear time-independent operator only while Eq. 4.0.5 is valid for square of the operator. In the above Eq. 4.0.5, \{\cdot\} represents an operator. The first term in Eq. 4.0.6 contains the kinetics as well. Thus, it accounts the kinetic effect of even simple reversible redox reaction. Also, Danckwerts’ expression for current is for planar case only while Eq. 4.0.6 is the generalized expression. This extension of Danckwert’s expression could prove useful in the study of pseudo first-order reaction mechanism at rough OTE-electrolyte interface.

\[ \langle A_{ga}(t) \rangle \] represents the expression for the purely diffusion-controlled reversible redox reaction and is given as [5]:

\[ \langle A_{ga}(t) \rangle = \frac{2 \epsilon C_0^0 \sqrt{Dt}}{\sqrt{\pi}} \left( 1 + \hat{R} \langle |\hat{\zeta}(K_{||})|^2 \rangle \right), \quad (4.0.7) \]

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

\[ \hat{R} = -\frac{1}{2(2\pi)^2} \int d^2 K_{||} \left( 1 - \exp(-K_{||}^2 Dt) - \sqrt{\pi K_{||}^2 Dt} \text{ erf} \left( \sqrt{K_{||}^2 Dt} \right) \right). \quad (4.0.8) \]

The moments of power-spectrum is related to the mean square derivatives of surface profile and give physical insights into the fractal rough surfaces. The 2j-th moments of power-spectrum of roughness is given as [48]:

\[ m_{2j} = \frac{1}{(2\pi)^2} \int d^2 K_{||} K_{||}^{2j} \langle |\hat{\zeta}(K_{||})|^2 \rangle = \langle (\nabla_{||}^j \zeta(r_{||}))^2 \rangle, \quad (4.0.9) \]

where \( \nabla_{||}^j \equiv (\partial/\partial x, \partial/\partial y) \) is the two dimensional gradient operator. The moments of power-spectrum are related to the various morphological features of a rough surface such as: mean square (MS) width \( (m_0) \), the MS gradient \( (m_2) \) and MS
curvature \((m_4)\). The surface roughness correlation function, power-spectrum and its moments are typically obtained from AFM studies.

5 OTE Surface as Band Limited Self-Affine Fractal

Many natural and artificial surfaces are characterized as self-affine fractal surfaces. The self-affine isotropic fractal surfaces are those surfaces in which isotropic profile functions remain statistically invariant under the scale transformation: 
\((x, y, z) \rightarrow (\lambda x, \lambda y, \lambda^H z)\) where \(H\) is the roughness Hurst’s exponent. Hurst’s exponent describes the persistence and anti-persistence behavior in the height fluctuation and is related to fractal dimension \((D_H)\) for isotropic self-affine surface as \(D_H = 3 - H\). Surfaces with limited scales of invariance property are usually described by the stationary, Gaussian random processes with a power-law spectrum over a limited range of wave-numbers \([53]\).

The roughness spectrum of an approximately self-affine isotropic (random) fractal surface is described in terms of a limited band of wave-numbers \((\vec{K}_\parallel)\) which follows a power-law function as \([54, 55]\):

\[
\langle |\hat{\zeta}(\vec{K}_\parallel)|^2 \rangle = \mu |\vec{K}_\parallel|^{2D_H-7}, \quad \frac{1}{L} \leq |K_\parallel| \leq \frac{1}{\ell}.
\] (5.0.1)

This description of roughness consists of four physical characteristics which describes the power-spectrum of roughness. Among them, fractal dimension \((D_H)\) is the global property of roughness and describes the scale invariance property of the rough surfaces. \(\ell\) and \(L\) are the lower and upper length scales of fractality, respectively. The lower roughness scale is the length above which surface shows fractal behavior. Similarly, \(L\) is the length below which surface show fractal behavior. The strength of fractality \((\mu)\) is related to the topothesy of fractal \([54, 55, 56]\) and \(\mu \rightarrow 0\) means no roughness. These realistic (finite) fractal characteristics can be obtained from AFM measurements on the surface and its power-spectrum. The idealized fractal description of anomalous power-law behavior in the current or
charge or absorbance-transient and their time exponent is simply assumed to be function of $D_H$ only.

The information related to the morphology with its physical significance can be obtained from moments of power-spectrum such as mean square width of interface ($m_0$), mean square gradient ($m_2$), mean square curvature ($m_4$) and so on. The general expression for the $2j$–th moment of the power-spectrum for a band-limited fractal can be written as [57]:

$$m_{2j} = \frac{\mu}{4\pi} \left( \frac{l^{-2(\delta + j)}}{\delta + j} - \frac{L^{-2(\delta + j)}}{\delta + j} \right),$$  \hspace{1cm} (5.0.2)

where $\delta = D_H - 5/2$.

The surfaces with small $m_2$ (i.e. small $\mu$) are referred as low roughness surfaces and surfaces with large $m_2$ (i.e. large $\mu$) as large roughness surfaces. The roughness factor gives the extent of the deviation of spectroelectrochemical responses (current, charge or absorbance) from the smooth surface. Therefore, the roughness factor for low roughness surfaces is given by $R^* \approx 1 + m_2$. Similarly, the roughness factor for large roughness surfaces is $R^* = \sqrt{\pi m_2/2}$.

The total interfacial ensemble averaged absorbance-transient for an EC' process is obtained by solving the Eq. 4.0.6 which is the general form of the absorbance-transient for rough electrode surfaces. Thus, the first term of the Eq. 4.0.6 is for the ensemble averaged absorbance-transient for the purely diffusion-limited reaction at an approximately self-affine fractal electrode surface which is given as [5]:

$$\langle A_{ga}(t) \rangle = A_P(t)(1 - R_{F1}(t) + R_{F2}(t, \ell) - R_{F2}(t, L))$$  \hspace{1cm} (5.0.3)

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

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

where $\lambda$ is the cut-off length (either $\ell$ or $L$) and 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 [44].

The Eq. 5.0.4 represents the exact form of the absorbance [5] because the first term of Eq. 4.0.6 can be integrated with respect to time. The second and the third terms of Eq. 4.0.6 have difficulty of integration with respect to the time with the exact form. This is due to the fact that these terms bring the kinetic contribution. Thus, to solve these two terms, an approximated form of the absorbance is used to overcome this difficulty for the longer time. The longer time is the kinetic control and this approximation works good for the longer time regime. So we use this approximation to solve the second and the third terms of Eq. 4.0.6. The expression for the approximate form of the absorbance used to solve these terms is given as [5]:

\[
\langle A_{ga}(t) \rangle \approx \frac{2}{\sqrt{\pi}} \frac{\epsilon C_0^0 \sqrt{D} t}{\sqrt{\pi}} \left(1 - \frac{\mu \ell^{-2\delta}}{8\pi \delta D t} + \frac{\mu \Gamma(\delta)}{8\pi (2\delta + 1)(D t)^{\delta + 1}}\right). \tag{5.0.4}
\]

The above Eq. 5.0.4 is valid for \( t \gg t_i \), where \( t_i \) is the inner fractal crossover time. It is the time after which the anomalous intermediate time regime is observed in the absorbance-transient. The short-time contribution to the total absorbance-transient, i.e. \( \langle A(t_i) \rangle \) is very small for all \( t \gg t_i \); hence, it is ignored in the above calculation.

After using Eq. 5.0.4, the second term (say \( A_1(t) \)) in the Eq. 4.0.6 takes the form as:

\[
A_1(t) = 2 k \int_0^t dt' e^{-k t'} \langle A_{ga}(t') \rangle
= \frac{2k}{\sqrt{\pi}} \left(2\epsilon C_0^0 \sqrt{D} \right) \left\{ \frac{\sqrt{\pi} \text{ erf} \left(\sqrt{kt}\right)}{2\sqrt{k^3}} - \frac{\sqrt{t} e^{-kt}}{k} - \frac{\mu \ell^{-2\delta} \sqrt{\pi} \text{ erf} \left(\sqrt{kt}\right)}{8\pi \delta D \sqrt{k}} \right. \left. - \frac{\mu \Gamma(\delta) k^{\delta - 1/2}\Gamma(1/2 - \delta, kt)}{8\pi (2\delta + 1) D^{\delta + 1}} \right\}, \tag{5.0.5}
\]

and the third term (say \( A_2(t) \)) in the Eq. 4.0.6 for self-affine fractal electrode
becomes as:

\[ A_2(t) = k^2 \int_0^t dt' \int_0^{t'} dt'' e^{-kt''} \langle A_{gy}(t'') \rangle \]

\[ = \frac{k^2(2 \epsilon C_0^0 \sqrt{D})}{\sqrt{\pi}} \frac{\sqrt{\pi} \text{erf} \left( \sqrt{kt} \right)}{2 k^{3/2}} \left( \frac{-3}{2k} + t \right) \]

\[ + \frac{3 \sqrt{t} e^{-kt}}{2 k^2} - \frac{\mu}{8 \pi D \sqrt{k}} \left( \frac{\sqrt{\pi} \ell^{-2\delta}}{\delta} \right) \left( \sqrt{\frac{t}{\pi k}} e^{-kt} \right) \]

\[ + \left( t - \frac{1}{2k} \right) \text{erf} \left( \sqrt{kt} \right) + \frac{\Gamma(\delta) k^\delta}{(2\delta + 1) D^\delta} \left( t \Gamma(1/2 - \delta, kt) - \frac{1}{k} \Gamma(3/2 - \delta, kt) \right) \]  

(5.0.6)

For the limiting case that is, at \( k = 0 \) the second and the third terms in the Eq. 4.0.6 becomes zero and it is reduced to the purely diffusion-controlled phenomena [5]. Under this condition, the Eq. 4.0.6 becomes same as Eq. 5.0.3 in chapter 2. Thus we can say that, Eq. 4.0.6 is also valid for the simple reversible redox systems (i.e. purely Nernstian case) under the limiting case. If the roughness is zero this equation reduces for purely diffusion-limited planar case (Eq. 1.0.2). Thus, Eq. 4.0.6 is very significant to study the EC’ reaction at rough OTE-electrolyte interface. It provides more physical insights into the EC’ reaction mechanism taking place at the rough electrode-electrolyte interface with proper characterisation of the rough surface morphology in terms of the fractal morphological characteristics.

6 Results and Discussion

Figure 3.1 depicts the various morphological and phenomenological characteristics which control the absorbance-transient response of an EC’ reaction mechanism at fractally rough OTE-electrolyte interface. The four morphological characteristics are fractal dimension \( (D_H) \), strength of fractality \( (\mu) \), lower \( (\ell) \) and upper \( (L) \) cut-off length scales. Out of these, \( D_H, \mu \) and \( \ell \) contribute strongly to the absorbance-transient while \( L \) shows weak dependency for large fractal range, \( \rho \) \( (= L/\ell \text{ ratio}) \). Here \( \sqrt{Dt} \) is known as the diffusion-width.
Figure 3.2: Effect of fractal dimension ($D_H$) on absorbance-transients while other parameters are kept constant. The values of $D_H$ (from bottom to top) are taken as: 2.10, 2.15, 2.20, 2.25. The other parameters used to generate the curves are as: $\ell = 50 \text{ nm}$, $L = 5 \mu \text{m}$, $\mu = 5 \times 10^{-6}(\text{a.u.})$, $k = 10 \text{ s}^{-1}$, $\epsilon = 10^4 \text{ cm}^2 \text{ mol}^{-1}$, $C^0_O = 5 \times 10^{-6} \text{ mol cm}^{-3}$, $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The first plot from bottom (black curve) is of planar response of the EC’ reaction mechanism (see Eq. 1.0.1).
Figure 3.3: Effect of strength of fractality (µ) on absorbance-transients while other parameters are kept constant. The values of µ (a.u.) (from bottom to top) are taken as: $5 \times \mu_0$, $10 \times \mu_0$, $20 \times \mu_0$, $40 \times \mu_0$ where $\mu_0 = 10^{-6}$. The other parameters used are as: $D_H = 2.20$, $\ell = 50 \text{ nm}$, $L = 5 \mu m$, $k = 10 \text{ s}^{-1}$, $\epsilon = 10^4 \text{ cm}^2 \text{ mol}^{-1}$, $C_0^0 = 5 \times 10^{-6} \text{ mol cm}^{-3}$, $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The first plot from bottom (i.e. black curve) is the response of the EC reaction mechanism at planar electrode (see Eq. 1.0.1).
Figure 3.4: Effect of lower cut-off length scale ($\ell$) on absorbance-transients while keeping other parameters constant. The values of $\ell (nm)$ (from top to bottom) are taken as: 25, 50, 100, 400. In this plot the other parameters used are as: $D_H = 2.20$, $\mu = 5 \times 10^{-6}$ (a.u.), $L = 5 \mu m$, $k = 10 \ s^{-1}$, $\epsilon = 10^4 \ cm^2 \ mol^{-1}$, $C_O^0 = 5 \times 10^{-6} \ mol \ cm^{-3}$, $D = 5 \times 10^{-6} \ cm^2 \ s^{-1}$. The first plot from the bottom (black curve) is of planar response for the EC’ reaction mechanism (see Eq. 1.0.1).
Figure 3.5: Effect of homogeneous rate constant ($k$) on absorbance-transients while other parameters are kept constant. The values of $k(s^{-1})$ are taken as (from bottom to top): 1, 10, 50, 100, 200. The other parameters used to generate this plot are as: $D_H = 2.20$, $\mu = 5 \times 10^{-6}(a.u.)$, $\ell = 50 \text{ nm}$, $L = 5 \mu m$, $\epsilon = 10^4 \text{ cm}^2 \text{ mol}^{-1}$, $C_O^0 = 5 \times 10^{-6} \text{ mol cm}^{-3}$, $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.
Figure 3.2 is the double logarithmic plot of absorbance and time. In this figure, the effect of fractal dimension ($D_H$) on absorbance-transients response is depicted. The various fixed morphological characteristics used to generate the curves are taken as: $\mu = 5 \times 10^{-6} (a.u.), \ell = 50 \text{ nm}, L = 5 \mu m$ and homogeneous rate constant is $k = 10 \text{ s}^{-1}$. This figure illustrates that, as the fractal dimension increases the catalytic absorbance-transient enhances. The first plot from bottom (i.e. black curve) is the response of the absorbance-transient for the EC’ reaction at planar OTE, i.e. without roughness (Eq. 1.0.1). The increase in fractal dimension means increase in roughness. Since the total effective area of the electrode increases due to roughness which catalyzes the redox reaction and concentration of the photoactive species increases thus, absorbance-transients enhance. There is a significant increase in absorbance-transient as compared to the planar response due to the increase in roughness. The plot clearly depicts two time regimes in it, i.e. anomalous intermediate and long-time. Out of these two time regimes, the anomalous intermediate region is most important as far as the effect of surface roughness on the absorbance-transient is concerned. The diffusion-layer width ($\sqrt{Dt}$) is comparable to the surface irregularities in the anomalous intermediate region hence, the diffusion-layer-width senses the irregularities which provides the information related to the surface roughness. In short time regime the diffusion-layer width is smaller than $\ell$ while in long time regime it is larger than $h$ (width of the interface) for the surface irregularities. Hence, the planar electrode response is observed in these two time regimes. The traditional plots ($A(t)$ vs $t^{1/2}$) do not show these time regimes which lacks the detailed morphological information related to the rough surfaces.

Figure 3.3 is the double logarithmic plot of absorbance and time while varying strength of fractality $\mu$ which is also known as topothesy and is proportional to the mean square width of the interface. The various fixed morphological characteristics are taken as: $D_H = 2.20, \ell = 50 \text{ nm}, L = 5 \mu m$ and homogeneous rate constant is $k = 10 \text{ s}^{-1}$. The increase in the strength of fractality increases the roughness while keeping other morphological characteristics constant. In early time, absorbance-transient enhances rapidly while intermediate regime shows weak dependency with time. Finally, it merges with the planar response in the long-time regime.
In Fig. 3.4 the effect of lower cut-off length scale ($\ell$) on absorbance-transients is shown while other parameters are kept constant. The various fixed morphological characteristics are taken as: $D_H = 2.20$, $\mu = 5 \times 10^{-6}$ (a.u.), $L = 5 \mu m$ and homogeneous rate constant is $k = 10 \text{ s}^{-1}$. The inner-transition time ($t_i$) is the time after which anomalous intermediate time regime is started. This comes in the region which is less than $10^{-3}$s. We have not considered the time region which is less than $10^{-3}$s in our calculation since below this time double-layer contribution becomes prominent which we have not accounted here in our calculations. The short-time domain is strongly dependent on the lower cut-off length scale ($\ell$) while long-time domain is controlled by width of the interface ($h$). The width of the interface is a strong function of upper cut-off length scale ($L$) and has no impact of lower cut-off length scale ($\ell$) in the long-time domain. Therefore, the inner transition-time ($t_i$) decreases with decrease in lower cut-off length scale ($\ell$) while it increases as the $\ell$ increases. The decrease in lower cut-off length scale increases the roughness as well as the self-affine fractal nature of the OTE surface consequently, absorbance-transients enhance. The anomalous intermediate regime shows weak dependency on time while in long-time regime it merges to the planar response (Eq. 1.0.1).

Figure 3.5 is double logarithmic plot of absorbance and time which depicts the effect of homogeneous rate constant $k$, on the absorbance-transients for an EC’ reaction mechanism. The various fixed morphological characteristics in this case are taken as: $D_H = 2.20$, $\ell = 50 \text{ nm}$, $L = 5 \mu m$, $\mu = 5 \times 10^{-6}$ (a.u.). Here, as the value of homogeneous rate constant increases, absorbance-transients also enhance prominently in the long-time regime. In the short-time domain there is no effect of homogeneous rate constant on absorbance-transients at fixed roughness factor except at the very high value of rate constant. As the value of homogeneous rate constant increases, first it shows no (especially at the lower values) or week dependency on absorbance-transient. Then it goes to a minimum and after this, it achieves the steady-state condition in the long-time regime. This minimum becomes more and more prominent as the value of the rate constant increases. The time at which this minimum arises, keep on decreasing as the rate constant increases and vice-versa. The appearance of minimum roughly corresponds to $1/k$. 

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value. Anomalous intermediate-time regime shows very weak dependency on rate constant. But the long-time domain shows strong dependency on rate constant and achieves the steady-state condition. The steady-state is achieved due to the catalytic effect. Thus, the long-time regime clearly demonstrates the time dependent kinetic controlled regime. The inset is the traditional plot \( \mathcal{A}(t) \ versus t^{1/2} \) of the corresponding double logarithmic curves. There are no characteristic features observed in this plot as the double logarithmic curves provide. Thus, we can observe the roughness effect clearly in the double logarithmic scale while it does not show any signature in the traditional plot.

7 Conclusions

The present paper enabled us to get insights into the effect of fractal nature of the OTE roughness (morphology) on absorbance-transient responses for an EC’ reaction mechanism. The following conclusions can be drawn here: (1) the absorbance-transients enhance as the roughness of the OTE surface increases, (2) the fractal nature of the rough OTE surfaces show localized reaction which enhances the absorbance-transient significantly, (3) the anomalous intermediate-time regime shows strong dependency on the fractal morphological characteristics, (4) the long-time regime is the time dependent kinetic controlled regime, (5) the traditional \( \mathcal{A}(t) \ versus t^{1/2} \) plots do not provide any signature related to the rough OTE-electrolyte interface and, (5) our ab-initio methodology based on the power-spectrum of roughness is able to characterize all the three time regimes in absorbance-transients successfully. Since in reality (intentionally or unintentionally) some roughness is always present at the solid electrode surface thus, this theoretical model provides a physical picture which relates the fractal morphological characteristics with absorbance-transient. Finally, the theory was an indispensable step in the quantitative description of the role of the roughness on absorbance-transient for an EC’ reaction mechanism at rough OTE-electrolyte interface.
Bibliography


