Chapter 3

Current transients across Electrode/Ionic Liquid Interface

Prelude
In this chapter we present an approximate theoretical model for diffusion-limited processes on realistic fractal interfaces and its use for the quantification of current responses corresponding to potential steps at electrode/RTIL interface. The model includes a complete set of realistic fractal morphological characteristics and gives information about various morphological features of electrode surface. A comparison of Cottrell equation with the present model to account for the experimentally recorded current transients across electrode/RTIL interface is also presented. The new result explains experimental findings of the temporal scale invariance as well as deviation from this in transition region with better accuracy than the conventionally used Cottrell equation.

3.1 Introduction

Current transients across electrode/electrolyte interface have proved to be very informative for electroanalytical investigations of heterogeneous electron transfer [1, 2]. Their use for estimation of transport and kinetic parameters is based on quantification of current-time and current-potential transients in terms of transport and kinetic parameters for the associated charge transfer. Development of theoretical treatments for these quantification procedures utilizing valid approximations, while involving maximum parameters of analytical significance has been a challenging task. Early treatments were mainly based on solution, geometrical and electrical characteristics of the interface neglecting the role of electrode morphology [1, 2]. The success of these theories based on strictly smooth electrode surface is attributed to facile diffusion process and the time scale of the measurements, leading to diffusion layer thickness much larger than the roughness scale of the reasonably polished electrodes [2]. Nevertheless, the characteristics of the electrode surface are exceptionally important for all electrochemical processes because they affect
ion adsorption/desorption reaction and charge transfer reaction which occur on the electrode/electrolyte interface.

A new addition to the use of current transients for understanding heterogeneous electron transfer, is the use of room temperature ionic liquids (RTILs) as solvents in electrochemical setups. Currently the use of RTILs as substitute of conventional solvents in electrochemical setups is receiving great attention. This is attributed to the electrochemical advantages of RTILs, like wide electrochemical window, appreciable electrical conductivity that abrogates the use of supporting electrolytes from electrochemical setups and their structural aspects that mimic features of sites for biological electron transfer [3–7]. The conclusions from the investigations related to RTIL based electrochemical setups, can be realistic only if the theories and approximations used for the electrode/RTIL interface in such studies are quite close to the actual.

Some special concerns need to be addressed while using conventional theories of current transients for such transients across electrode/RTIL interface. Since RTILs are considered as structured solvents [4], the upper time limit on account of possible convection is low as compared to conventional solvents. An additional concern is the low diffusion coefficients of analytes in RTILs [4, 7], leading to small diffusion field thickness and hence making electrode roughness features more significant. Hence for electron transfer at electrode/RTIL interface, electrode roughness is expected to play a more significant role than in conventional solvents due to comparable diffusional length and scale of electrode roughness. To our knowledge in all the published reports about heterogeneous electron transfer at electrode/RTIL interface, smoothness of electrode especially for GC is always one of the approximations. Nevertheless, it is an accepted fact that even with all the precautions taken for smoothening the electrode surface, roughness is always a feature associated with all electrodes. However, usually the analysis is based on approximation that on the practical time scale, the diffusion layer thickness minimizes or almost erases the impact of electrode roughness in conventional electrochemistry. The same can not be true in case when RTILs are used in place of conventional solvents in electrochemical setups. In this regard, electrochemical interfaces involving RTILs are a new challenge to the surface chemist, electrochemist and theoretician. Several theories have been proposed and tested for explaining and understanding the solution side of electrode/RTIL
interface [8–11], but the realistic picture of electrodes is yet to be fully understood, especially vis-a-vis the impact of surface roughness of electrode on phenomena associated with these interfaces. Several workers have used the concept of fractals to quantify the impact of complexity arising out of electrode roughness morphology [12–30]. In light of these reports and the above mentioned concerns, it seems that the concept of fractals is more significant for electrode/RTIL interface.

Glassy carbon (GC) is the commonly used electrode in interfaces designed to understand heterogeneous electron transfers especially those related to biological systems. The common advantages responsible for its frequent use are (i) its ability to allow outer-sphere electron transfer reactions [31] (ii) availability of several simple and reliable procedures to clean and reproduce its surface conditions, and (iii) its ability to provide soft landing for biologically important molecules like-enzymes, proteins etc [32]. Aim of our work presented in the current chapter was to explore the impact of surface roughness of approximated smooth GC electrode on current transients for species dissolved in RTILs. The work gains importance in view of the present trend about electrochemistry related research implying RTILs.

The chapter is divided in two sections: (i) an approximate theoretical model is presented for the quantification of the current transient on irregular electrode/electrolyte interface. Here interfacial irregularity is modeled as a realistic random fractal, which is characterized as statistically isotropic self-affine fractals on limited length scales. The power spectrum of such a surface fractal is approximated in terms of a power law function for the intermediate wave numbers and, (ii) the applicability of the developed statistical model for the quantification of current transients at GC/RTIL and metal/RTIL interfaces is tested.

3.2 Theoretical

The recent years experimental advances in physical methods like: scanning probe microscopy [33], electron diffraction [34], X-ray reflectivity [35] and gas adsorption [36] have provided new insights for comprehensive understanding and visualization of solid
surfaces at atomic level. Transient response in potential controlled experiments is a reliable procedure which can yield information about many electrochemical processes. Especially in heterogeneous surface chemistry, the characterization of the rough surfaces using fractal geometry plays a vital role in understanding the anomalous behavior of rough surfaces and interfaces. Irregularity due to interfacial roughness is commonly modeled as a surface fractal [12–30]. Recently Kant and co-workers [12, 13, 21] have proposed realistic fractal morphological model which constitutes not only elegant description of the surface roughness but is also a very versatile and generally implementable one. They have modeled the interfacial irregularity in terms of power spectrum of roughness. The complexity in transport phenomena due to several morphological length scales and phenomenological length scales can be understood through a schematic diagram of a disordered working electrode as shown in Figure 3.1. The interfacial irregularity is modeled with power spectrum of roughness. The four fractal morphological characteristics are: fractal dimension \(D_H\), lower \(\ell\) and upper \(L\) cutoff length scales of fractality, and the proportionality factor \(\mu\) related to topothesy or strength of fractality [15].

The mathematical formulation of the diffusion limited interfacial reaction on disordered surface has complexity associated with boundary condition on surface with uncontrolled

\[ \text{Figure 3.1: Schematic diagram of a randomly rough electrode/RTIL interface, where the charge transfer reaction } O + ne^- \rightarrow R \text{ is occurring under diffusion-controlled condition. The phenomenological length scale is diffusion layer thickness } (L_D = \sqrt{Dt}) \text{ and the random roughness profile is characterized by four roughness characteristics } \text{viz., the mean square width } (h^2) \text{ which is proportional to the strength of fractality } (\mu), \text{ lower cutoff length scale } (\ell), \text{ upper cutoff length scale } (L), \text{ and the fractal dimension } (D_H). \]
surface geometric disorder. The complete diffusion problem under the diffusion limited charge transfer process (for a reaction, $O + ne^- \rightleftharpoons R$) satisfies the equation

$$\frac{\partial}{\partial t}C_\alpha(\vec{r}, t) = D_\alpha \nabla^2 C_\alpha(\vec{r}, t)$$  \hspace{1cm} (3.1)$$

where $\alpha \equiv O, R$, representing the oxidized or reduced species, $D_\alpha$ is diffusion coefficient (for simplicity, we assume in our calculations $D_O = D_R = D$) and $\vec{r}$ is the three dimensional vector, $\vec{r} \equiv (x, y, z)$. At initial time and far off from the interface, a uniform initial and bulk concentration, $C^0$ is maintained viz. $C_\alpha(\vec{r}, t = 0) = C_\alpha(z \rightarrow \infty, t) = 0$. There is a local transfer kinetics limitation at the interface ($\zeta$) and this is represented by the Nernstian boundary condition

$$C_s = \delta C_O(z = \zeta(\vec{r}), t) = -\frac{C^0_O - C^0_R\theta}{1 + \theta}$$  \hspace{1cm} (3.2)$$

where $\delta C_\alpha(\zeta)$ is the difference between surface and bulk concentration, $\theta = \exp(-nf(E_i - E_o'))$, $E_i$ and $E_o'$ are the initial and formal potential, respectively. $F$ is Faraday’s constant, $f = F/RT$, $R$ is the gas constant and $T$ is temperature. The excess surface concentration $C_s$ can be identified as a function of the impressed constant potential assuming Nernstian behavior. The formalism to solve this random boundary value problem is described in references [25, 26]. Here we use this formalism for a realistic random fractal roughness that is statistically isotropic. When a potential step is applied at a flat electrode, the time dependence of faradaic current $I_p(t)$ is well described by the Cottrell equation [2]

$$I_p(t) = nF A_0 D^{1/2} C_s \sqrt{\pi t}$$  \hspace{1cm} (3.3)$$

where $A_0$ is the projected area of the surface, $C_s$ is the excess surface concentration of electrolyte solution through Nernstian equation, $D$ is the diffusion coefficient, $n$ is the number of electron transferred and $F$ is the Faraday constant. In the case of a fractal electrode, the relationship between current and time follows generalized Cottrell equation popularized by Nyikos and Pajkossy based upon the scaling law for current

$$I(t) \sim t^{-\beta}$$  \hspace{1cm} (3.4)$$

where the exponent $\beta$ depends on interfacial roughness. Theoretical justification for equation 3.4 was provided by De Gennes scaling result [19] with $\beta = (D_H - 1)/2$ and
generalized form [30]. But these approaches have limitations as they are unable to include a complete set of realistic fractal morphological characteristics and use assumption that fractal dimension is the sole feature to characterize ‘realistic’ fractal surface for comprehensive understanding of dynamic response of the interface. Particularly, difficulties arise in the transition region and often mix data of the scaling region with the transition region and hence there is an inaccurate prediction of fractal dimension.

The specific form of the roughness function depends on the morphology of the interface. For an isotropic fractal surface, the information about surface roughness enters in this theory through power spectrum of roughness. The power spectrum of a realistic surface (also called “approximate self-affine fractal”) is described in term of limited scales of wave-numbers ($K$) power-law function [37, 38]

$$\left\langle \hat{\zeta}(\mathbf{K}) \right\rangle^2 = \mu |K|^{2D_H-7}, \text{ for } 1/L \leq |K| \leq 1/\ell.$$  \hspace{1cm} (3.5)

This power spectrum of roughness has four morphological characteristics of roughness, namely $D_H, \ell, L$ and $\mu$. The fractal dimension, $D_H$ is a global property which describes scale invariance property of the roughness- an anomalous behavior in current response and its time exponent is usually assumed to be function of this characteristic. The minimum length scale above which surface shows fractal roughness is represented by lower cutoff length scales of fractality ($\ell$), the upper cutoff length scales of fractality ($L$) and $\mu$ is the strength of fractal which is related to topothesy of fractals [39], its dimension is $[\text{Length}]^{2D_H-3}$ and $\mu \to 0$ implies no roughness. The moments of power-spectrum are related to various morphological features of rough surface viz. rms width ($\sqrt{m_0}$), rms gradient ($\sqrt{m_2}$), rms curvature ($\sqrt{m_4}$) etc. The general moments of power spectrum (i.e., 2k-th moments, $m_{2k}$) are easily obtained for above mentioned power-spectrum and are important morphological characteristic of surface roughness. The general formula is:

$$m_{2k} = \mu \left( \ell^{-2\delta_k} - L^{-2\delta_k} \right) / 4\pi \delta_k$$ \hspace{1cm} (3.6)

where $\delta_k = \delta + k$ and $\delta = D_H - 5/2$. The roughness factor ($R^*$) is a dimensionless measure of surface morphology (= average area/projected area). The roughness factor (i) for low roughness surfaces i.e., small $m_2$ (small $\mu$), $R^* \approx 1 + m_2/2$, (ii) for intermediate roughness surfaces, $R^* \approx 1 + \sqrt{m_2} U(1/2, 1/2, 1/2m_2)$ where $U(a, b, z)$ is a confluent hypergeometric function [40] and (iii) for large roughness surfaces i.e., large $m_2$ (large
The mathematical formalism for the diffusive flux/current at random rough surfaces is well described in terms of power spectral density of roughness \( \left\langle \left| \hat{\zeta}(\vec{K}) \right|^2 \right\rangle \) [25, 26]. We used this approach and made an approximation for the derivation by the truncation of solution at second order in surface roughness profile. The total (averaged) current at the stationary, Gaussian random surface is given by [25, 26]:

\[
\left\langle I(t) \right\rangle = \frac{nFD^{1/2}A_0C_s}{\sqrt{\pi t}} \left[ 1 + \frac{1}{4\pi Dt} \int_0^\infty dKK \left( 1 - e^{-K^2Dt} \right) \left\langle \left| \hat{\zeta}(\vec{K}) \right|^2 \right\rangle \right]
\]

(3.7)

where \( A_0 \) is the area of surface around which rough surface fluctuates. The diffusion controlled reaction current is related to the potentiostatic current transients of an electrode undergoing fast charge transfer. The anomalous diffusive reaction rates on realistic self-affine fractals are obtained by using the exact solution for the dynamic diffusive flux on an approximate self-affine surface. Substituting equation 3.5 for band-limited power law spectrum in equation 3.7 and solving resultant integral, we obtained the following equation:

\[
\left\langle I(t) \right\rangle = I_p(t) \left( 1 + \frac{\mu}{8\pi} \left( \frac{\ell^{-2\delta} - L^{-2\delta}}{\delta Dt} \right) + \frac{\Gamma(\delta, Dt/\ell^2, Dt/L^2)}{(Dt)^{1+\delta}} \right)
\]

(3.8)

where \( \delta = D_H - 5/2, \Gamma(\alpha, x_0, x_1) = \Gamma(\alpha, x_0) - \Gamma(\alpha, x_1) = \gamma(\alpha, x_1) - \gamma(\alpha, x_0), \Gamma(\alpha, x_i) \) and \( \gamma(\alpha, x_i) \) are the incomplete Gamma functions [40]. The graphical analysis of equation 3.8 has been already presented in reference [12] and these calculations break the earlier beliefs based on idealized fractal models that the exponent of anomalous diffusion region purely depends on fractal dimension of roughness. These calculations clearly demonstrate that the exponent of the anomalous region is dependent on all three dominant fractal morphological characteristics. It is important to note that equation 3.8 is valid in all time regimes.

Generally experimental data are recorded for the intermediate and long time regime \( t > \sim \ell^2/D \). So for these types of electrode reaction system, we have expanded the two incomplete gamma functions in equation 3.8 viz., one for small \( Dt/L^2 \) and another for large \( Dt/\ell^2 \) (see appendix for these expansions) and retaining only leading orders [40]. Final equation has a simple and elegant form as follows:

\[
\left\langle I(t) \right\rangle \approx I_p(t) \left[ 1 + R_I(t) \right]
\]

(3.9)
where

\[ R_I(t) = \frac{\mu}{4\pi(5 - 2D_H)} \left( \frac{\Gamma(D_H - 3/2)}{(Dt)^{(D_H - 3/2)}} - \frac{\ell^{-(2D_H - 5)}}{Dt} \right) \]

where \( R_I(t) \) is the generalized roughness contribution to the current response in the anomalous regime or intermediate scaling regime. All of these mathematical functions can be easily evaluated through any standard software like: Origin, Mathematica, Matlab, etc. Equations (3.8) and (3.9) extend the conventional representation of the Cottrell current transient \( (1/\sqrt{t}) \) on the planar electrode in electrochemistry [2] to the fractally rough electrode. These equations achieve a more realistic approach for statistical characterization of limited scale rough surface diffusive flux as it includes the fractal dimension dependent power law as well as contribution from the length scale and strength of fractality \( (\mu) \). The total mean current is the summation of planar electrode response and an anomalous excess current due to fractal roughness or can also be looked upon as product of the \( 1/\sqrt{t} \) current and dynamic roughness factor (term inside parenthesis of equations 3.8 and 3.9). In this study, equation 3.9 is used for statistical characterization of fractally rough glassy carbon electrode/room temperature ionic liquid interface and predicting various morphological informations.

### 3.3 Experimental

#### 3.3.1 Chemicals

Chemicals used were of Analytical Reagent grade. Acetonitrile and ethyl acetate were purchased from Merck, India. 1-methylimidazole, 1-chlorobutane and hexafluorophosphoric acid (62% aqueous solution) were procured from Spectrochem India. Ferrocene was purchased from Sigma-Aldrich. Tetrabutyl ammonium perchlorate (TBAP) was purchased from Across Organics.

#### 3.3.2 Synthesis of \([\text{BMIM}][\text{PF}_6]\)

‘Voltammetrically pure’ ionic liquid, having low background currents was synthesized using a reported method [41]. Gordon et al. recommendations [42] have been used for the purification of the starting materials, conditions for quaternization reactions, anion exchange reaction and finally purification of RTILs. 1-butyl-3-methylimidazolium
chloride was prepared through quaternization reaction of 1-methylimidazole with 1-chlorobutane under Ar atmosphere as discussed elsewhere [43]. [BMIM][PF$_6$] was synthesized through anion exchange reaction of [BMIM][Cl] with hexafluorophosphoric acid. For the anion exchange reaction, 25.0 g of freshly prepared [BMIM][Cl] was dissolved in 150.0 mL millipore water. The solution was ice cooled and into it, hexafluorophosphoric acid (44.0 mL) was added drop wise with a continuous stirring. Two immiscible phases were formed which were stirred continuously for an hour. The aqueous phase was decanted and the organic phase was repeatedly washed with ice cooled millipore water till the washings were no more acidic. The product was then dissolved in dichloromethane to which, 2.0 mg activated charcoal and 20.0 mg anhydrous Na$_2$SO$_4$ were added with a brisk warming. After an hour, the organic phase was filtered out and dried under the vacuum at 75 °C. A colorless liquid whose NMR spectrum matched well with that reported for [BMIM][PF$_6$] was obtained [44]. The liquid was stored in a polypropylene bottle under the vacuum dried conditions. Storage in borosilicate glass bottles was particularly avoided due to the appearance of noxious fumes followed by accumulation of a white solid in the storage bottle. This is attributed to HF etching and the generation of volatile silicon fluoride and acid, which forms due to hydrolysis of PF$_6^-$ in a moist environment [45].

### 3.3.3 Electrochemical measurements

All CV and chronoamperometric measurements were performed using a computer controlled Metrohm PGSTAT100 Potentiostat/Galvanostat in a three electrode setup. A thermostatted (± 0.1 °C) and airtight jacket glass cell having an arrangement to place the electrodes at a distance of 5 mm from one another was designed. Prior to the experiment, the cell was immersed in 2M HNO$_3$ for 24 hours, rinsed thoroughly with copious amount of Millipore water and dried at 60 °C in an oven. All the measurements were carried out in an inert atmosphere. For that, Ar gas was passed continuously through the solution for ca. 15 minutes. Moreover, the measurements were performed under the Ar blanket. Ag wire (99.9%) and platinum (99.9%) mesh were used as a quasireference (QRE) and counter electrode respectively. Prior to use, these were washed with dilute
HNO₃ and then rinsed with copious amount of Millipore water. A glassy carbon electrode (GC) of geometric area (0.031 cm²) was used as working electrode, which was gently polished over Alumina powder (0.25 µm size), rinsed with jet of millipore water and wiped with soft tissue paper soaked in ethanol.

Though ionic in nature, [BMIM][PF₆] is resistive electrolyte in normal electrochemical terms. Thus, the voltammograms were observed to be distorted due to significant uncompensated resistance between the reference and working electrode. Therefore, inbuilt positive feedback circuitry was used to evaluate and compensate the solution resistance.

Electrochemical experiments for estimation of redox and kinetic characteristics were carried at high concentrations of ferrocene (25 mM) in view of expected low diffusion coefficients in a viscous medium of ionic liquids. All the CV data was background corrected prior to the analysis. Chronoamperometric experiments were carried out for a polarization duration of 10 s. The current values were sampled with time interval of 0.05 s. Data for time period up to five times of that of time constant of $R_u C_d$ (obtained from potential step experiments in nonfaradaic region) was discarded to minimize the contribution from the nonfaradaic processes. Data fitting was performed using inbuilt and some written subroutines in the software package Origin 6.0 (Microcal Software Inc.).

3.4 Results and discussion

![Figure 3.2](image)

**Figure 3.2:** (A) Background corrected experimental cyclic voltammograms (scan rate = 50 mVs⁻¹) (B) CVs recorded at varying scan rates (50-1000 for mVs⁻¹), for 25 mM ferrocene in [BMIM][PF₆] at 298 K. GC as working and Ag wire as quasireference electrode (QRE) were used. Inset in Figure 3.2(B) depicts plot for $I_p$ vs. square root of scan rate of the recorded CVs.
A typical CV recorded for ferrocene in [BMIM][PF₆] is depicted in Figure 3.2A. CVs were recorded at changing scan rates from 0.05-1.0 V s⁻¹, these are depicted in Figure 3.2B. The observed peak width slightly greater than that expected for a typical reversible reaction, is perhaps because positive feed back method could not fully compensate for the IR drop. In the scan rate investigated, peak current was a linear function of square root of scan rate (as depicted in inset of Figure 3.2), which implies diffusion controlled nature for redox process of ferrocene. Once the CV characteristics were analyzed, chronoamperometric measurements were performed. Current transient corresponding to the potential step to diffusion controlled limit of CV in Figure 3.2A is shown in Figure 3.3. Figure also shows the comparison between fits from equation 3.3, 3.9 and experimental data. Current transient corresponding to the potential step to diffusion controlled limit was processed iteratively according to eq. 3.9, using algorithm based on Livenberg marquadt method. Figure 3.3 depicts an excellent agreement between experimental and theoretical data (as per eq. 3.9). The fit parameters viz. diffusion coefficient of ferrocene (D), $D_H$, $\ell$, $L$ and $\mu$ were evaluated. The value of $\chi^2$ i.e., the error between the experiment points and the theoretical curve, is considered as fitting indicator: the lower $\chi^2$, the better the fit. 

The parameters were collected after 500 iterations, after which these values were found not to change with statistical fit parameter values, $\chi^2 = 1.6135\times10^{-14}$, $R^2 = 0.99958$. This

Figure 3.3: Current transient for potential step to diffusion controlled electrolysis of 25 mM ferrocene in [BMIM][PF₆] on GC electrode. (a) experimental (b) fit as per eq. 3.3 (c) fit as per eq. 3.9.
much magnitude of $\chi^2$ implies a negligible difference between the experimental and theoretical values. Based on the magnitude of these values, we calculated the width of the interface ($h$), root mean square gradient ($\sqrt{m_2}$), inverse root mean square curvature ($r_c = 1/\sqrt{m_4}$), and roughness factor ($R^*$), the values are enlisted in table 3.1. The result-

Table 3.1: Electrode morphological Characteristics of GC from the diffusion controlled current transient of ferrocene (25 mM) on GC/[BMIM][PF$_6$] interface at 298 K

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_H$</td>
<td>2.09354</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$8 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\ell$</td>
<td>3.1 $\mu$m</td>
</tr>
<tr>
<td>$L$</td>
<td>20 $\mu$m</td>
</tr>
<tr>
<td>$D$</td>
<td>$2.133 \times 10^{-7}$ cm$^2$s$^{-1}$</td>
</tr>
<tr>
<td>$h$</td>
<td>2.796 $\mu$m</td>
</tr>
<tr>
<td>RMS gradient</td>
<td>0.37</td>
</tr>
<tr>
<td>Inverse RMS curvature</td>
<td>12.843 $\mu$m</td>
</tr>
<tr>
<td>Roughness factor</td>
<td>1.13</td>
</tr>
</tbody>
</table>

The observed value of diffusion co-efficient $viz.$ $2.13 \times 10^{-7}$ cm$^2$s$^{-1}$ matches very well with those reported earlier [46]. As seen from the value of $h$, the value is much higher than the values seen in case of conventional organic solvent electrochemistry, this is well expected as per the double layer structure reports in RTILs [8–11] and is perhaps the reason for lower values of electron transfer rate constants in RTILs. Clearly the magnitude of parameters signifying the electrode roughness, warrant that the assumption of smoothness for GC is erroneous for current transients at GC/RTIL interface.

We also verified our theoretically calculated roughness factor value from chronoamperometric data with that obtained from CVs. From the CVs recorded using Randles-Sevcik equation the roughness factor value, $R^* = 1.1258$ was estimated, which approximately matches with the value obtained while processing current transient data by using equation 3.9. The advantage we see with the present formulation is that with a single equation (equation 3.9), surface and geometry characteristics of electrode in addition to the diffusion coefficient of the electroanalyte can be obtained. This is advantageous in comparison to the conventional Cottrell equation, where in only information about the diffusion coefficient is the end-result of analysis.
3.4.1 Current transients across metal/RTIL interface

We also recorded the chronoamperometric current transients across metal/RTIL interface for ferrocene in [BMIM][BF₄], to test the advantage of equation 3.9 over that of equation 3.3 for simulating the experimental trend. For this a 2 mm diameter Pt disk and 2 mm diameter Au disk electrode, cleaned mechanically, chemically and electrochemically as per procedures presented in reference [32] were used as working electrodes. The current transients were recorded in a 20 mM solution of ferrocene in [BMIM][BF₄], in a manner similar to as followed in case for GC electrode. The resulting experimental data and their fits using equation 3.3 and 3.9 are presented in Figure 3.4A for Pt and Figure 3.4B for Au electrode. As seen clearly, the equation 3.9 simulates the experimental data better than the Cottrell equation 3.3.

![Figure 3.4](image)

**Figure 3.4:** Experimental, fit as per equation 3.3 and 3.9 current transient for potential step to diffusion controlled electrolysis of 20 mM ferrocene in [BMIM][PF₆] on (A) Pt, (B) Au as working electrode

3.5 Conclusions

The present work was devoted to have a better understanding of electrode interfacial irregularity on current response with the goal of predicting various morphological features. The applicability of this theory is discussed for quantification of current transients at GC/RTIL interface. There is a very good agreement of this model with experimental data Figure (3.3). The most remarkable investigation here is the value of diffusion coefficient (D) which matches very well with the earlier reported value [46]. The experimentally determined roughness factor value is exactly matching with our theoretically
predicted value. The anomalous scaling behavior in the intermediate time regime shows
the power law behavior of current and the plots are dependent on fractal dimension, lower
cutoff length scale, and the strength of fractality. Physical reasons for these observations
is that the diffusion length is comparable to the size of surface roughness features. Some
of the earlier attempts are mainly based on numerical approach in steady state response
or scaling approach of idealized fractal model. The direct influence on all time response
of rough electrode with characteristic fractal roughness parameters like - fractal dimen-
sion ($D_H$), strength of fractality ($\mu$) and cutoff lengths (lower cutoff length $\ell$ and upper
cutoff length $L$) are never understood simultaneously. Finally, this theory offers a solu-
tion to long-standing problem of diffusion limited process across an irregular electrode
and gains importance in view of the present trend about electrochemistry related research
implying RTILs.

**APPENDIX**

The small $z$ expansion for the incomplete gamma functions [40] is

$$
\Gamma(a, z) = \Gamma(a) - z^a \sum_{n=0}^{\infty} \frac{(-z)^n}{(a+n)n!}
$$

(3.10)

The large $z$ asymptotic expansion for the incomplete gamma function [40] is

$$
\Gamma(a, z) \sim z^{a-1} e^{-z} \left[ 1 + \frac{a-1}{z} + \frac{(a-1)(a-2)}{z^2} + \ldots \right]
$$

(3.11)
References


[16] Sapoval, B. In Fractal electrodes, fractal membranes and fractal catalyst in Fractals and disordered systems; Bunde, A., Havlin, S., Ed.; Springer-Verlag, Heidelberg, 1996.


