Anomalous fluctuations in current transient at glassy carbon|room temperature ionic liquid interface

Mohsin Ahmad Bhat*, Shailendra K. Jha**

Department of Chemistry, University of Pune, Ganeshkhind, Pune 411007, India

ABSTRACT

Here we report the theory and experimental study of anomalous diffusion phenomena coupled with facile charge transfer reaction at fractally rough glassy carbon|room temperature ionic liquid (GC|RTIL) interface. A finite self-affine scaling property has been exhibited by a realistic fractal electrode surface. A comparison of classical Cottrell equation with the present theoretical model to account for the experimentally recorded current transients across GC|RTIL interface is also presented. This model gives information about various morphological features of electrode surface. An excellent correspondence of calculated and reported diffusion coefficient is also obtained.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Current transients across electrode|electrolyte interface in potential controlled experiments are considered as one of the reliable procedures for estimation of transport and kinetic parameters associated with electrochemical processes [1,2]. Development of approximate theoretical treatments for quantification of current–time and current–potential transients in terms of the relevant kinetic and transport parameters has been a challenging task since many decades. Theoretical treatments put forward so far in this regard are mainly based on solution, geometrical and electrical characteristics of the interface wherein the role of electrode morphology is totally neglected [1,2]. The success of these theories which are based on strictly smooth electrode surface is attributed to facile diffusion process and the time scale of the measurements, that lead to diffusion layer thickness which is larger than the roughness scale of the reasonably polished electrodes [2]. Nevertheless, the characteristics of the electrode surfaces are exceptionally important for all electrochemical processes because they do affect ion adsorption/desorption reaction and charge transfer reactions which occur on the electrode|electrolyte interface. Since past few decades electrochemists world over have been paying a

considerable attention towards the fundamental and applied aspects of charge transfer processes in room temperature ionic liquid (RTIL) based electrochemical setups. In fact on account of their inherent advantageous electrochemical features, *viz.*, wide electrochemical window, appreciable conductivity, ability to selectively stabilize the electrogenerated species, structural aspects that mimic features of sites for biological electron transfer, RTILs are now increasingly being used as a safe, green and innovative substitute to conventional solvents in electrochemical investigations [3–9]. In all the reports published so far in this regard, it has been approximated that conventional theories that have been developed and tested over years for the conventional solvent systems are equally valid for RTIL based setups. 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 in RTILs is expected to be lower than that observed in conventional solvents. An additional concern is the low diffusion coefficients of analytes in RTILs [4,7], that leads to small diffusion field thickness wherein the contribution due to electrode roughness features should be appreciable. In this regard, electrochemical interfaces involving RTILs present a new challenge to the surface chemist, electrochemist and theoretician. While several theories have been proposed and tested for explaining and understanding the solution side of electrode|RTIL interface [10–13], very little attention [14] has been paid to understand the impact of electrode morphology on the various characteristics associated with these interfaces. Several workers have used the concept of fractals to quantify the impact of complexity arising out of electrode roughness morphology [14–31]. In light of these

* Corresponding author. Present address: Department of Chemistry, University of Kashmir, Srinagar 190006, India. Tel.: +91 194 2424900x27; fax: +91 194 2421357.
** Corresponding author. Present address: Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu, India.
E-mail addresses: mohsinch@kashmiruniversity.ac.in, mohsin_skb@yahoo.co.in (M.A. Bhat), skjha@cecri.res.in (S.K. Jha).

reports and the above mentioned concerns, it seems that the concept of fractals is more significant for electrode|RTIL interface. Aim of our work presented in the current paper was to explore the impact of surface roughness of approximated smooth electrode on Faradaic current transients observed for species dissolved in RTILs. The paper 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 interfaces is tested. Glassy carbon (GC) was chosen since it is the most 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 [32], (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. [33]. The presented work gains importance in view of the structural organization prevailing in the bulk and RTILs confined to interfaces [34,35], that make them suitable solvent systems that can be explored for arriving at a comprehensive understanding of electron transfers in biological systems.

2. Theoretical

Fractal geometry approaches wherein the irregularity due to interfacial roughness is commonly modeled as a surface fractal [14–31] have been successfully employed for exploring and understanding the anomalous behavior of rough surfaces and interfaces in heterogeneous surface chemistry. Kant and co-workers [15–17,23] have proposed a realistic fractal morphological model to explain the transient responses from rough interfaces. An adequate roughness parameter was assumed to be fractal dimension till-date, which accounts both the vertical and the lateral information of three-dimensional surfaces over a significant range of length scales. For this analysis scanning probe microscope (SPM) is a more adequate technique than scanning electron microscope (SEM) and transmission electron microscope (TEM) because of the three-dimensional digitized image of the surface morphology. We can directly describe the surface morphology by the digitized height data with a resolution down to the atomic scale by usage of a scanning tunneling microscope (STM) and an atomic force microscope (AFM). Several algorithms have been developed and used to determine surface fractal dimension from SPM images. But the power spectrum method has become the most popular and reliable one.

With the above mentioned motivation, interfacial irregularity has been modeled in terms of power spectrum of roughness. The role of complexity in transport phenomena due to morphological length scales and phenomenological length scales and to understand the rationale in their operation are depicted in the schematic diagram, i.e., Fig. 1. The interfacial irregularity is modeled with power spectrum of roughness. The four fractal morphological characteristics are: fractal dimension (D_H), lower (ℓ) and upper (L) cutoff length scales of fractality, and the topothesy length (μ) [18]. Quantitative modeling and analysis have to take the same considerations. Here we derive an analytical expression that quantifies the consequences of dynamic fractal roughness to the current transient. The mathematical formulation of the diffusion limited interfacial reaction on disordered surface has complexity associated with boundary condition on surface with
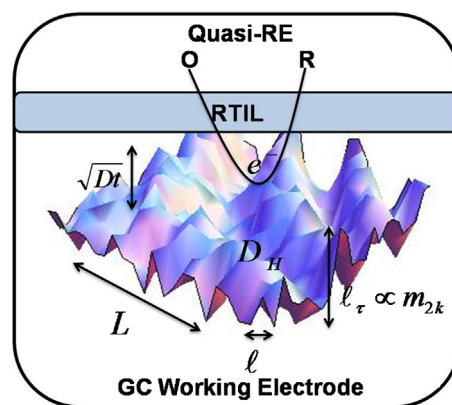

Fig. 1. Schematic diagram of a randomly rough electrode|RTIL interface, where the charge transfer reaction $O + ne^- \rightleftharpoons R$ is occurring under diffusion-controlled condition. The phenomenological length scale is diffusion layer thickness ($\sqrt{Dt}$) and the random roughness profile is characterized by four roughness characteristics, viz., the topothesy length (ℓ_τ) which is proportional to the moments of power spectrum (m_{2k}), lower cutoff length scale (ℓ), upper cutoff length scale (L), and the fractal dimension (D_H).

uncontrolled surface geometric disorder. The complete diffusion problem under the diffusion limited charge transfer process (for a reaction, $O + ne^- \rightleftharpoons R$) must satisfy the equation

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

where $\alpha \equiv O, R$, representing the oxidized or reduced species, D_α 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^o is maintained, viz., $C_\alpha(\vec{r}, t = 0) = C_\alpha(\vec{r}_\parallel, z \to \infty, t) = 0$, where $\vec{r}_\parallel \equiv (x, y)$. There is a local transfer kinetics limitation at the interface (ζ) and this is represented by the Nernstian boundary condition

$$-C_s = \delta C_O(z = \zeta(\vec{r}), t) = -\frac{C_O^0 - C_R^0 \theta}{1 + \theta} \tag{2}$$

where $\delta C_\alpha(\zeta)$ is the difference between surface and bulk concentration, $\theta = \exp(-nf(E_i - E^{0'}))$, E_i and $E^{0'}$ are the initial and formal potential, respectively. F is Faraday's constant, $f = F/RT$, R is a gas constant and T is temperature. Under Nernstian condition, the excess surface concentration C_s is a function of the impressed constant potential. The problem addressed here has similar kind of mathematical isomorphism as reported elsewhere [15,16,26,27]. The similar mathematical structure but different physical problems have been formulated here.

When a potential step is applied to a flat electrode, the time dependence of Faradaic planar electrode current $I_p(t)$ can be expressed by the classical Cottrell equation [2]

$$I_p(t) = \frac{nFA_0 D^{1/2} C_s}{\sqrt{\pi t}} \tag{3}$$

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 electrons transferred. Nyikos and Pajkossy [36,37] have popularized the concept of fractal to understand the complex systems in electrochemistry based on the scaling law for current: $I(t) \sim t^{-\beta}$, where the exponent, β depends on interfacial roughness. Theoretical justification of scaling concept was provided in De Gennes scaling result [21] with $\beta = (D_H - 1)/2$ and generalized form [31]. The assumption was that fractal dimension characterize 'realistic' fractal surface and can be used for comprehensive understanding of dynamic response of the