



General Theory for Pulse Voltammetric Techniques on Rough and Finite Fractal Electrodes for Reversible Redox System with Unequal Diffusivities



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ARTICLE INFO

Article history:

Received 12 December 2015
Received in revised form 4 February 2016
Accepted 7 February 2016
Available online 11 February 2016

Keywords:

Pulse Voltammetry
Differential Pulse Voltammetry
Square Wave Voltammetry
Unequal Diffusion Coefficients
Finite Fractal Electrodes

ABSTRACT

The prediction of voltammetric response from the microscopic information of the electrode surface morphology is an important problem of fourth generation electrochemistry which we have theoretically addressed here. We develop a theory for pulse based voltammetric response of reversible charge transfer process with unequal diffusivities on randomly rough electrode. The microscopic information of the electrode surface is incorporated into the response expression in the form of power spectrum of roughness. An elegant expression for the statistically averaged generalized pulse voltammetric current is obtained in terms of single potential step current at rough electrode from which, the explicit current expressions for differential pulse (DPV), staircase (SCV), cyclic staircase (CSCV) and square wave (SWV) voltammetries are obtained for random and finite fractal roughness electrode. The SCV and CSCV responses, as elaborately discussed in our previous work, here we have focused more on the explorations of DPV and SWV responses. In the presence of equal diffusion coefficients of the electroactive species, roughness induces enhancement in the peak heights with retention of peak position at the same potential for DPV as well as SWV. This points towards an enhanced sensitivity of these differential techniques at rough electrodes. In the presence of unequal diffusivities of redox species, SWV shows a distinguished signature of roughness due to variation in peak heights along with alteration in the position of the peaks. Square wave voltammetry on rough electrode shows an asymmetric suppression in the peak height of the anodic or cathodic sampled current plots due to unequal diffusivities which resembles the behavior of a chemically irreversible system.

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1. Introduction

Pulse based voltammetric techniques form an area of intense research which has been reviewed many times since last two decades [1–7]. This is attributed to the tremendous development in the fields of fundamental understanding as well as applications of these techniques with the evolution of various new pulse sequences and current sampling patterns. Depending on the requirement, for instance, achievement of better charging current discrimination, higher sensitivity, ease of application of the perturbing potential pulse sequence and interpretation of the response signal, some of these techniques are preferred over others under different circumstances. Though, voltammetries have many advantages, these are also affected by a number of factors like other electrochemical techniques which include electrode roughness, solution resistance,

adsorption occurring at the electrode, viscosity of the solution etc. Usually, various precautionary measures are taken to control the phenomena such as solution resistance and adsorption; an important aspect which is often neglected by the experimentalists is the influence of electrode roughness on the voltammetric measurements. The extensive use of solid metal electrodes, screen printed electrodes, electrodes modified with nanoparticles, films etc. in fundamental and applied systems demand further development of the classical understanding with inclusion of the electrode roughness in the models.

Most of the attempts made to model the voltammetric response of rough electrodes are limited to LSV and CV techniques [8–11]. In 2008, Compton et al used a computational approach to predict the CV response of an electrode having regular array of bell shaped protrusions [11]. Due to consideration of the oversimplifying assumption of independent diffusion domains of each peak and length scales of larger magnitude than that of the diffusion layer thickness, the model could not unravel the anomalous influence of electrode roughness on the response voltammograms. Moreover,

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such ideal (one length scale) roughness is seldom found at realistic electrodes. Solid electrodes undergoing various cleansing processes often give rise to random fractal roughness on the electrode surface. Various approaches used to model the voltammetric response of the random fractal roughness electrodes are based on fractional diffusion [12–14], scaling argument [15–17,10], numerical simulations [8,9] and ab-initio [18–20] approaches. In the fractional diffusion and scaling argument approaches the only requisite parameter for electrode characterization is the fractal dimension (D_H). Though the number of parameters in a theory is always a concern for experimentalists, the electrode characterization exclusively through D_H makes these one parameter theories more suitable for idealized fractal roughness which is seldom found in the realistic systems. The anomalous electrochemical response of realistic electrodes is also controlled by statistical cut-off length scales of the fractality and roughness amplitude along with the fractal dimension without accrediting which, D_H remains as a fitting parameter. These characteristics of the electrode morphology can be easily accessed from the roughness power spectrum [21–23] which in turn can be obtained from various surface microscopies, viz. AFM, SEM, STM etc.

In 2010, a model based on ab-initio methodology, containing a general formalism applicable to any arbitrary potential based voltammetric and chronoamperometric techniques was developed by Kant [18]. This approach successfully relates the electrochemical response of any arbitrary and random roughness electrode to the morphological information obtained from microscopy techniques [23,22,20,21]. Using ab-initio approach, Kant and coworkers have established a series of relations between electrode morphology and various electrochemical responses, viz. chronoamperometry [24–27], chronocoulometry [28], admittance [29,30], impedance [31–34], absorbance [35] and voltammetry [18–20]. The current expression deduced for an arbitrary potential sweep technique at a rough electrode is given by [18]:

$$\langle I(t) \rangle = \frac{d}{dt} \int_0^t \tilde{\chi}_0(t-t') \langle I_{gc}(t') \rangle dt' \quad (1)$$

where, $\langle I_{gc}(t) \rangle$ represents the current transient for single potential step for any arbitrary random roughness electrode [36]:

$$\langle I_{gc}(t) \rangle = I_C(t) \left(1 + \frac{1}{2(2\pi)^2 Dt} \int d^2 K_{\parallel} \left(1 - e^{-K_{\parallel}^2 Dt} \right) \langle |\tilde{\zeta}(\vec{K}_{\parallel})|^2 \rangle \right) \quad (2)$$

where, $I_C(t)$ is Cottrell current given by:

$$I_C(t) = \frac{nFA_0\sqrt{DC_s}}{\sqrt{\pi t}} \quad ; \quad C_s = \frac{C_O^0 - \theta C_R^0}{1 + \theta} \quad (3)$$

where, $\theta = e^{-nf(E_i - E^0)}$; $f = F/RT$; E_i and E^0 representing applied potential and formal potential, respectively; C_O^0 and C_R^0 , the bulk concentrations of oxidized and reduced species; A_0 , geometrical area of electrode; n , number of electrons transferred; F , Faraday's constant; R , gas constant; T , absolute temperature, D represents the diffusion coefficient (for simplicity, it is assumed that diffusion coefficients of reduced and oxidized species are equal i.e. $D_O = D_R = D$) and $\tilde{\chi}_0$ is given by:

$$\tilde{\chi}_0(t) = \frac{\chi_0(t)}{-C_s} = \frac{1 - \frac{C_O^0}{C_O^0 - C_R^0} \theta (e^{-\sigma g(t)} - 1)}{1 + \frac{\theta}{1+\theta} (e^{-\sigma g(t)} - 1)} \quad ; \quad \sigma = nfv \quad (4)$$

The function $g(t)$ represents the time dependent part of the potential perturbation. Thus, $\chi_0(t)$ is basically the difference between surface and bulk concentration, i.e., $C_O(0, t) - C_O^0$, which can be obtained from Nernst condition with the assumption

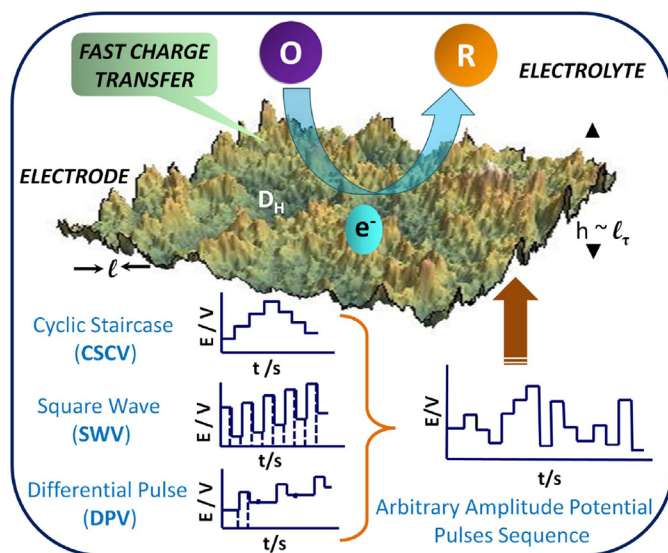


Fig. 1. Schematic of the problem for a reversible charge transfer under an arbitrary potential pulses sequence modulation applied at the rough electrode. Finite fractal roughness characteristics which dominantly control the response are fractal dimension (D_H), lower cut-off length scale of fractality (l) and topothesis length (l_τ) which is related to h (width of interface).

$D_O = D_R = D$ which simplifies to the condition that sum of concentrations of oxidized and reduced species is constant for any distance and time.

$$\chi_0(t) = -\frac{C_O^0 - C_R^0 \theta e^{-\sigma g(t)}}{1 + \theta e^{-\sigma g(t)}} \quad (5)$$

Thus, as apparent from Eq. (4), $\tilde{\chi}_0$ contains the non-geometric information and is purely dependent on initial concentration and potential components. In order to further solve the integral present in the equation numerical routes are required for the continuous time based techniques. However, for the pulse based techniques the analytical route is exploited by Kant et al [19,20] to deduce the response expressions for staircase and cyclic staircase voltammeters.

Now, we wish to deduce a general result applicable for any sequence and amplitude of pulses (see Fig. 1). Commonly, in ionic liquids [39,20], in the presence of chelating ligands [40,41] and in low polarity solvents like THF [42] the electroactive species are observed to have significant difference in their diffusivities. Accordingly, we develop a general formalism which corrects for the case of unequal diffusion coefficients of the electroactive species. The paper is organized as follows: initially, the mathematical formulation for the problem of pulse voltammetry at any arbitrary profile electrode is presented and the explicit expression for current transient is obtained which is then discussed in detail for isotropic (self-affine) finite fractal electrode. Effects of various morphological characteristics on the voltammograms are explored.

2. Mathematical Formulation

Semi-infinite mass transport for a single charge transfer step, $O + ne^- \rightleftharpoons R$, is expressed by following partial differential equation

$$\frac{\partial}{\partial t} C_\alpha(\vec{r}, t) = D_\alpha \nabla^2 C_\alpha(\vec{r}, t) \quad (6)$$

where $C_\alpha(\vec{r}, t)$ is the concentration profile with α representing the oxidized (O) or reduced species (R), D_α is the diffusion coefficient, $\nabla^2 \equiv (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ and $\vec{r}$ represents the 3-D vector, $\vec{r} \equiv (x, y, z)$. A uniform initial and bulk concentration $C_\alpha(\vec{r}, t)$ is

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