



# Theory of Double Potential Step Chronoamperometry at Rough Electrodes: Reversible Redox Reaction and Ohmic Effects



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## ABSTRACT

Theory is developed for the DPSC (double potential step chronoamperometry) response for finite fractal and nonfractal electrode roughness with and without uncompensated solution resistance. Mathematical equation for the statistically averaged current transient and its relation to surface structure factor of random roughness is highlighted for reversible charge transfer. Result shows the enhancement of current transient upto outer crossover time for the rough electrode. Current response after application of each potential steps can show upto three regimes, i.e. short, intermediate and long time regimes. In short time, when diffusion layer thickness is small, current response is controlled by the roughness factor. Crossover between short and intermediate time regimes is controlled by diffusion layer thickness scaled with mean square surface curvature. Current behavior in long time (after outer crossover time), when diffusion layer thickness is large compared to width of roughness, becomes identical to smooth electrode. Crossover between intermediate and long time regimes is controlled by mean square width scaled with diffusion layer thickness. For fractal roughness, current has anomalous power law behavior (in intermediate time regime) while for nonfractal roughness current shows crossover between two regimes. Increase in the ratio of reverse and forward current is usually understood as kinetic complications but here we show that this can also emerge out of electrode roughness. Uncompensated solution resistance correction is also included in our theory to account for realistic experimental conditions. Finally, results are compared with the experimental data of a reversible system in viscous medium.

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## 1. Introduction

Double potential step chronoamperometry (DPSC) is an effective approach to investigate electrochemical processes taking place at an electrode/electrolyte interface. DPSC has been a widely used electroanalytical technique for evaluation of quantity like concentration, diffusion coefficients, rate constants of homogeneous reactions, activation and inactivation rate constants of enzymes [1–3]. This technique offers criteria for determining whether kinetic currents are involved or not in an electrode process, to study adsorbed species on electrode surface, and is an excellent tool for the study of different types of mechanisms [2,4–7]. DPSC can be used for the quantitative determination of the migrational contribution to the current transient measured for redox systems [8]. DPSC is a powerful technique for the study of chemical reactions

following the electrode reaction, reactant and product adsorption at conventional-sized electrodes. A major characteristic of the method, is that the faradaic and charging currents can be easily separated [2,9–11]. Advantage of using DPSC than single potential step chronoamperometry allows simultaneous determination of the diffusion coefficients of the initial species, and the product of the electrochemical reaction [12]. This method is used extensively in applied systems like batteries, fuel cells, electrochromic films, bio-electrochemistry, water electrolysis etc. [6,13–18].

DPSC is special case of the result first obtained by Kambara [19,20]. For a reversible charge transfer system  $O + ne^- \rightleftharpoons R$  occurring at electrode/electrolyte interface, current transient response for DPSC at planar electrode is described under semi-infinite linear diffusion condition. The current for forward step of diffusion limited process or Nernstian case at planar electrode/electrolyte interface is [10]:

$$I_f(t) = \frac{nFA_0D_0C_0^0}{\sqrt{\pi D_0 t(1 + \xi\theta_f)}} \quad (1)$$

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$A_0$	Geometric area
$C_\alpha^0$	Bulk concentration of the oxidized species e.g. $\alpha=O$ , R
$C_s$	Surface concentration for forward step using Nernst equation
$C_p$	Surface concentration for reverse step using Nernst equation
$\delta C_O$	Change in concentration of oxidized species
$CR^{Smooth}(t)$	Ratio of forward and reverse current for smooth electrode
$CR(t)$	Ratio of forward and reverse current for rough electrode
$D_i$	Diffusion coefficient of i-th species e.g. $i=O, R$
$D_H$	Fractal dimension
$E(t)$	Time dependent potential of the working electrode
$E_f$	Potential of the working electrode at forward step
$E_r$	Potential of the working electrode at reverse step
$E^0$	Formal Potential
F	Faraday's constant
$\mathcal{F}$	Dynamic ohmic loss function at smooth electrode
$\mathcal{F}^*$	Dynamic ohmic loss function at rough electrode
$\langle H^2 \rangle$	Mean square curvature of roughness
$h$	Width of interface
$\langle I_{gc}(t) \rangle$	Generalized Cottrell current at rough electrode
$I_C(t)$	Cottrell current
$I_f(t)$	Forward step current at smooth electrode
$I_r(t)$	Reverse step current at smooth electrode
$I(t)$	Total current transient at smooth electrode
$\langle I_f(t) \rangle$	Forward step current at rough electrode
$\langle I_r(t) \rangle$	Reverse step current at rough electrode
$\langle I(t) \rangle$	Total current transient at rough electrode
$I_{C\Omega}(t)$	Current at smooth electrode with ohmic contribution
$\langle I_{a\Omega}(t) \rangle$	Current at rough electrode with ohmic contribution
$j$	Current density
$L_\Omega$	Diffusion-resistance length for forward step
$L_\Omega^r$	Diffusion-resistance length for reverse step
$\ell$	Lower cutoff length scale of a band-limited fractal
$\ell_\tau$	Topothesy length
$L$	Upper cutoff length scale or correlation length
$m_0$	Zerth moment of power spectrum
$m_2$	Second moment of power spectrum
$n$	Number of electrons transferred
$\vec{r}$	Vector (x, y, z)
$\vec{r}_\parallel$	Vector (x, y)
$R_\Omega$	Solution resistance
R	Gas constant
$R_F(t)$	Dynamic roughness function for finite fractal surfaces
$R_{nF}$	Dynamic roughness function for nonfractal surfaces
$R_{C\Omega}$	Dynamic roughness contribution coupled with ohmic effects
$R^*$	Roughness factor
$t$	Time
$t_0$	Step size
$t_o$	Outer crossover time
$t_i$	Inner crossover time
$t_r$	Reverse step time
$t_f$	Forward step time
T	Temperature
$u(t)$	Unit step function
z	Coordinate representing distance away from electrode

$\frac{\int d^2K_\parallel}{\Delta E}$	$\frac{\int dK_x \int dK_y}{(E_r - E_f)}$
$\xi$	$\sqrt{D_O/D_R}$
$\tilde{\zeta}(\vec{r}_\parallel)$	Arbitrary surface profile
$\nabla_\parallel$	$\hat{i}\partial_x + \hat{j}\partial_y$
$\langle  \tilde{\zeta}(\vec{K}_\parallel) ^2 \rangle$	Power spectral density
$\delta(t)$	Delta function
$\delta$	$D_H - 5/2$
$\sigma$	$nF\Delta E/(RT)$
$\tilde{\chi}_r(t)$	$C_p/C_s$
$\Gamma, \gamma$	Incomplete Gamma function
$\mu$	Strength of proportionality
$\theta_\beta$ ( $\beta=f, r$ )	$\exp[-nF(E_\beta - E^0)/RT]$

and the current during the reversal step is [10]:

$$-I_r(t) = \frac{nFA_0D_0C_0^0}{\sqrt{\pi D_0}} \left\{ \left( \frac{1}{1 + \xi\theta_f} - \frac{1}{1 + \xi\theta_r} \right) \left( \frac{1}{\sqrt{t-t_0}} \right) - \frac{1}{(1 + \xi\theta_f)\sqrt{t}} \right\} \quad (2)$$

where  $n$  is the number of electrons transferred in the reaction,  $F$  is Faraday's constant,  $A_0$  is projected area of the surface,  $C_0^0$  is the bulk concentration of oxidized species and  $t_0$  is time period of each step,  $\xi$  is  $\sqrt{D_O/D_R}$ ,  $D_O$  and  $D_R$  are the diffusion coefficient of oxidized and reduced species,  $\theta_\beta$  is  $\exp[-nF(E_\beta - E^0)/RT]$  where subscript  $\beta$  is  $f$  or  $r$ , representing forward and reverse step potential perturbation, respectively,  $R$  is the gas constant and  $T$  is the temperature. This representation of  $\theta_\beta$  is different from the representation given in reference by Bard [10] (where  $\theta_\beta = \exp[nF(E_\beta - E^0)/RT]$ ). In both representations positive net current taken as cathodic but in our representation when  $(E_\beta - E^0)$  becomes more positive, cathodic current increases while in Bard's representation when  $(E_\beta - E^0)$  becomes more negative, cathodic current increases. Difference in representation does not lead to any difference in current measurements. Bard representation of  $\theta_\beta$  can be achieved by multiplying potential difference  $(E_\beta - E^0)$  with negative sign. Using "unit step function ( $u(t)$ )" [21] current for forward and reverse step can be written collectively as

$$I(t) = I_f(t)(u(t) - u(t - t_0)) + I_r(t)u(t - t_0) \quad (3)$$

where unit step function [21] is defined as

$$u(t) = \begin{cases} 1 & \text{for } t > 0 \\ 0 & \text{for } t \leq 0 \end{cases}$$

Current  $I(t)$  will be equal to  $I_f(t)$  for time  $t \leq t_0$  and  $I(t)$  will be equal to  $I_r(t)$  for time  $t > t_0$ .

DPSC has been studied at various geometries (e.g. planar, spherical DME, SMDE and HMDE, microhemisphere, microdisk electrodes, UMEs etc. [24,1,4,5,11,12,22,23]). Above listed results are derived by considering that above mentioned solid geometries are smooth and electrode surface does not have any surface heterogeneity. Solid planar electrodes are not smooth, they exhibit complex surface morphology with varying degree of irregularity ranging from nanometer to micrometer length scales. Such complex unconventional geometrical disorder known to influence the electrode response [25–27]. The recent interest in surface disorder and finite fractal geometry has helped to understand the influence of electrode disorder on its response. Influence of roughness has been extensively studied on single potential step perturbation on chronoamperometric response [25–31]. Single potential

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